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Search Results -

| Term | Documents |
|---|-----------|
| TEMPERATURE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2280891 |
| TEMP.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 771544 |
| TEMPS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 79432 |
| TEMPERATURES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 655826 |
| HEAT\$4 | 0 |
| HEAT.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2400792 |
| HEATA.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 13 |
| HEATAAT.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| HEATABL.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| HEATABLE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 11855 |
| HEATABLY.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 33 |
| (L21 AND (TEMPERATURE OR HEAT\$4)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 6 |

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EPO Abstracts Database
Derwent World Patents Index
IBM Technical Disclosure Bulletins

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L23

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Search History

DATE: Monday, April 14, 2003 [Printable Copy](#) [Create Case](#)

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side by side

Hit Count Set Name
result set

DB=USPT,PGPB,JPAB,EPAB,DWPI,TDBD; PLUR=YES; OP=ADJ

| | | | |
|------------|---|--------|------------|
| <u>L23</u> | L21 and (temperature or heat\$4) | 6 | <u>L23</u> |
| <u>L22</u> | L21 and (relaxometer or relaxometry) | 1 | <u>L22</u> |
| <u>L21</u> | L20 and (water with oil) | 6 | <u>L21</u> |
| <u>L20</u> | L19 and (water) | 9 | <u>L20</u> |
| <u>L19</u> | L16 and (oil) | 13 | <u>L19</u> |
| <u>L18</u> | L17 and (heavy with (oil or water or fluid)) | 1 | <u>L18</u> |
| <u>L17</u> | L16 and (emuls\$9) | 6 | <u>L17</u> |
| <u>L16</u> | L15 and (oil or water or hydrogeneous or connate or fluid\$5) | 53 | <u>L16</u> |
| <u>L15</u> | L14 and (low\$4 or high\$4 or standard or averag\$4) | 54 | <u>L15</u> |
| <u>L14</u> | L13 and (spectr\$6 or amplitude or value or index\$3) | 54 | <u>L14</u> |
| <u>L13</u> | L12 and (cutoff or cut-off or "cut off" or threshold\$4) | 54 | <u>L13</u> |
| <u>L12</u> | L11 and (weight\$4 or heavy) | 168 | <u>L12</u> |
| <u>L11</u> | L10 and (transverse or "spin-spin" or "spin spin" or "t2" or "t.sub.2" or relax\$8) | 342 | <u>L11</u> |
| <u>L10</u> | L1 and ((low with field) with ((magnetic adj resonance) or MRI or NMR)) | 753 | <u>L10</u> |
| <u>L9</u> | L8 and (low\$4 or high or standard) | 3 | <u>L9</u> |
| <u>L8</u> | L7 and (spectr\$4 or amplitude or value or index\$3) | 3 | <u>L8</u> |
| <u>L7</u> | L6 and (emuls\$9) | 3 | <u>L7</u> |
| <u>L6</u> | L5 and (transverse or longitudinal or "spin-lattice" or "spin-spin" or "spin spin" or "spin lattice" or "t2" or "t.sub.2" or "t.sub.1" or "t1" or relax\$8) | 16 | <u>L6</u> |
| <u>L5</u> | L4 and (weight\$4 or heavy) | 16 | <u>L5</u> |
| <u>L4</u> | L3 and (cutoff or cut-off or "cut off" or threshold\$4) | 19 | <u>L4</u> |
| <u>L3</u> | L2 and (oil or water or hydrogeneous or connate or fluid\$5) | 65 | <u>L3</u> |
| <u>L2</u> | L1 and (relaxometer or relaxometry) | 82 | <u>L2</u> |
| <u>L1</u> | ((magnetic adj resonance) or MRI or NMR) | 145490 | <u>L1</u> |

END OF SEARCH HISTORY

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Search Results - Record(s) 1 through 3 of 3 returned.

☐ 1. Document ID: US 20030009297 A1

L9: Entry 1 of 3

File: PGPB

Jan 9, 2003

PGPUB-DOCUMENT-NUMBER: 20030009297
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|-----------------------|---------|-------|---------|---------|
| Mirochnik, Konstantin | Calgary | | CA | |
| Allsopp, Kevin | Calgary | | CA | |
| Kantzas, Apostolos | Calgary | | CA | |
| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|--------|------|
| Draw Desc | Image | | | | | | | | | | |

☐ 2. Document ID: US 5260050 A

L9: Entry 2 of 3

File: USPT

Nov 9, 1993

US-PAT-NO: 5260050
DOCUMENT-IDENTIFIER: US 5260050 A

TITLE: Methods and compositions for magnetic resonance imaging comprising superparamagnetic ferromagnetically coupled chromium complexes

DATE-ISSUED: November 9, 1993

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney, David F. | Dallas | TX | 75234 | |

US-CL-CURRENT: 424/9.351; 424/617, 424/9.35, 436/173, 436/806, 536/102, 536/112, 536/122, 556/61, 600/420

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|--------|------|
| Draw Desc | Image | | | | | | | | | | |

☐ 3. Document ID: US 5213788 A

L9: Entry 3 of 3

File: USPT

May 25, 1993

US-PAT-NO: 5213788

DOCUMENT-IDENTIFIER: US 5213788 A

**** See image for Certificate of Correction ****

TITLE: Physically and chemically stabilized polyatomic clusters for magnetic resonance image and spectral enhancement

DATE-ISSUED: May 25, 1993

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney; David F. | Dallas | TX | 75234 | |

US-CL-CURRENT: 424/9.322; 424/617, 424/9.35, 436/173, 436/806, 514/56, 514/836, 600/420

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|--------|------|
| Draw Desc | Image | | | | | | | | | | |

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| Term | Documents |
|--|-----------|
| HIGH.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 5220660 |
| HIGHS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1950 |
| STANDARD.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1030677 |
| STANDARDS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 162506 |
| LOW\$4 | 0 |
| LOW.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 3154003 |
| LOWA.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 48 |
| LOWABLE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 19 |
| LOWAC.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 6 |
| LOWACID.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 4 |
| LOWACK.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 31 |
| (L8 AND (LOW\$4 OR HIGH OR STANDARD)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 3 |

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Search Results - Record(s) 1 through 6 of 6 returned.

☐ 1. Document ID: US 20030009297 A1

L17: Entry 1 of 6

File: PGPB

Jan 9, 2003

PGPUB-DOCUMENT-NUMBER: 20030009297

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|-----------------------|---------|-------|---------|---------|
| Mirotnich, Konstantin | Calgary | | CA | |
| Allsopp, Kevin | Calgary | | CA | |
| Kantzas, Apostolos | Calgary | | CA | |
| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Draw Desc | Image | | | | | | | | | |

☐ 2. Document ID: US 6417326 B1

L17: Entry 2 of 6

File: USPT

Jul 9, 2002

US-PAT-NO: 6417326

DOCUMENT-IDENTIFIER: US 6417326 B1

TITLE: Fusogenic liposomes

DATE-ISSUED: July 9, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------|------------|-------|----------|---------|
| Cullis; Pieter R. | Vancouver | | | CA |
| Choi; Lewis S. L. | Burnaby | | | CA |
| Monck; Myrna | Vancouver | | | CA |
| Bailey; Austin L. | Washington | DC | | |

US-CL-CURRENT: 530/324; 530/326; 530/327

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Draw Desc | Image | | | | | | | | | |

☐ 3. Document ID: US 6123920 A

L17: Entry 3 of 6

File: USPT

Sep 26, 2000

US-PAT-NO: 6123920

DOCUMENT-IDENTIFIER: US 6123920 A

TITLE: Superparamagnetic contrast media coated with starch and polyalkylene oxides

DATE-ISSUED: September 26, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------------------------|-------|-------|----------|---------|
| Gunther; Wolfgang H. H. | Wayne | PA | | |
| Fujii; Dennis Kiyoshi | Wayne | PA | | |
| Kellar; Kenneth Edmund | Wayne | PA | | |
| Black; Christopher Douglass Valiant | Wayne | PA | | |
| Desai; Vinay C. | Wayne | PA | | |
| Beeber; Marshal | Wayne | PA | | |
| Wellons; Jennifer | Wayne | PA | | |
| Fahlvik; Anne Kjersti | Oslo | | | NO |
| N.ae butted.vestad; Anne | Oslo | | | NO |

US-CL-CURRENT: 424/9.322

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Drawn Desc | Image | | | | | | | | | |

☐ 4. Document ID: US 5336762 A

L17: Entry 4 of 6

File: USPT

Aug 9, 1994

US-PAT-NO: 5336762

DOCUMENT-IDENTIFIER: US 5336762 A

**** See image for Certificate of Correction ****

TITLE: Polychelating agents for image and spectral enhancement (and spectral shift)

DATE-ISSUED: August 9, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney; David F. | Dallas | TX | | |

US-CL-CURRENT: 534/16; 424/9.323, 424/9.35, 536/102, 536/112, 536/121, 536/122, 556/138, 556/45, 556/57

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Drawn Desc | Image | | | | | | | | | |

☐ 5. Document ID: US 5310539 A

L17: Entry 5 of 6

File: USPT

May 10, 1994

US-PAT-NO: 5310539
DOCUMENT-IDENTIFIER: US 5310539 A
**** See image for Certificate of Correction ****

TITLE: Melanin-based agents for image enhancement

DATE-ISSUED: May 10, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Williams; Robert F. | San Antonio | TX | | |

US-CL-CURRENT: 424/9.34; 424/9.35, 424/9.36, 424/9.361, 424/9.364, 523/375

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 6. Document ID: US 5155215 A

L17: Entry 6 of 6

File: USPT

Oct 13, 1992

US-PAT-NO: 5155215
DOCUMENT-IDENTIFIER: US 5155215 A
**** See image for Certificate of Correction ****

TITLE: Polychelating agents for image and spectral enhancement (and spectral shift)

DATE-ISSUED: October 13, 1992

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney; David F. | Dallas | TX | | |

US-CL-CURRENT: 534/16; 536/112, 536/113, 536/121, 536/17.1, 536/21, 536/51

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

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| Term | Documents |
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| EMULS\$9 | 0 |
| EMULS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 75 |
| EMULSA.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 5 |
| EMULSABLE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| EMULSAGEN.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| EMULSAMINE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 6 |
| EMULSAN.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 97 |
| EMULSANASE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2 |
| EMULSANOSOL.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2 |
| EMULSANOSOLS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| EMULSANS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 37 |
| (L16 AND (EMULS\$9)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 6 |

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Search Results - Record(s) 1 through 1 of 1 returned.

☐ 1. Document ID: US 20030009297 A1

L18: Entry 1 of 1

File: PGPB

Jan 9, 2003

PGPUB-DOCUMENT-NUMBER: 20030009297

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|-----------------------|---------|-------|---------|---------|
| Mirotnich, Konstantin | Calgary | | CA | |
| Allsopp, Kevin | Calgary | | CA | |
| Kantzas, Apostolos | Calgary | | CA | |
| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
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| Term | Documents |
|---|-----------|
| HEAVY.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 606042 |
| HEAVIES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1208 |
| HEAVYS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 10 |
| OIL.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1043379 |
| OILS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 201326 |
| WATER.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2784622 |
| WATERS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 56614 |
| FLUID.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1130980 |
| FLUIDS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 244547 |
| (17 AND (HEAVY WITH (OIL OR FLUID OR WATER))).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 1 |
| (L17 AND (HEAVY WITH (OIL OR WATER OR FLUID))).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 1 |

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Search Results - Record(s) 1 through 9 of 9 returned.

☐ 1. Document ID: US 20030009297 A1

L20: Entry 1 of 9

File: PGPB

Jan 9, 2003

PGPUB-DOCUMENT-NUMBER: 20030009297
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|-----------------------|---------|-------|---------|---------|
| Mirotnich, Konstantin | Calgary | | CA | |
| Allsopp, Kevin | Calgary | | CA | |
| Kantzas, Apostolos | Calgary | | CA | |
| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
| Draw Desc | Image | | | | | | | | |

KWIC

☐ 2. Document ID: US 20020167314 A1

L20: Entry 2 of 9

File: PGPB

Nov 14, 2002

PGPUB-DOCUMENT-NUMBER: 20020167314
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020167314 A1

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

PUBLICATION-DATE: November 14, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|------------------|------------|-------|---------|---------|
| Prammer, Manfred | Downington | PA | US | |

US-CL-CURRENT: 324/303

| | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
| Draw Desc | Image | | | | | | | | |

KWIC

☐ 3. Document ID: US 6512371 B2

L20: Entry 3 of 9

File: USPT

Jan 28, 2003

US-PAT-NO: 6512371

DOCUMENT-IDENTIFIER: US 6512371 B2

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

DATE-ISSUED: January 28, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|------------|-------|----------|---------|
| Prammer; Manfred | Downington | PA | | |

US-CL-CURRENT: 324/303

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 4. Document ID: US 6140817 A

L20: Entry 4 of 9

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 5. Document ID: US 5387865 A

L20: Entry 5 of 9

File: USPT

Feb 7, 1995

US-PAT-NO: 5387865

DOCUMENT-IDENTIFIER: US 5387865 A

TITLE: Permeability determination from NMR relaxation measurements for fluids in porous media

DATE-ISSUED: February 7, 1995

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------------|-------------|-------|----------|---------|
| Jerosch-Herold; Michael | High Bridge | NJ | | |
| Thomann; Hans | Bedminster | NJ | | |

US-CL-CURRENT: 324/303; 324/300

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Drawn Desc | Image | | | | | | | | | |

☐ 6. Document ID: US 5370901 A

L20: Entry 6 of 9

File: USPT

Dec 6, 1994

US-PAT-NO: 5370901

DOCUMENT-IDENTIFIER: US 5370901 A

TITLE: Compositions for increasing the image contrast in diagnostic investigations of the digestive tract of patients

DATE-ISSUED: December 6, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|--------------------|----------|-------|----------|---------|
| Tournier; Herve | Valleiry | | | FR |
| Hyacinthe; Roland | Douvaine | | | FR |
| Cavagna; Friedrich | Vicenza | | | IT |

US-CL-CURRENT: 427/212; 424/95, 427/214, 436/173

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Drawn Desc | Image | | | | | | | | | |

☐ 7. Document ID: US 5336762 A

L20: Entry 7 of 9

File: USPT

Aug 9, 1994

US-PAT-NO: 5336762

DOCUMENT-IDENTIFIER: US 5336762 A

**** See image for Certificate of Correction ****

TITLE: Polychelating agents for image and spectral enhancement (and spectral shift)

DATE-ISSUED: August 9, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney; David F. | Dallas | TX | | |

US-CL-CURRENT: 534/16; 424/9323, 424/935, 536/102, 536/112, 536/121, 536/122, 556/138, 556/45, 556/57

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Drawn Desc | Image | | | | | | | | | |

☐ 8. Document ID: US 5310539 A

L20: Entry 8 of 9

File: USPT

May 10, 1994

US-PAT-NO: 5310539

DOCUMENT-IDENTIFIER: US 5310539 A

**** See image for Certificate of Correction ****

TITLE: Melanin-based agents for image enhancement

DATE-ISSUED: May 10, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Williams; Robert F. | San Antonio | TX | | |

US-CL-CURRENT: 424/9_34; 424/9_35, 424/9_36, 424/9_361, 424/9_364, 523/375

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 9. Document ID: US 5155215 A

L20: Entry 9 of 9

File: USPT

Oct 13, 1992

US-PAT-NO: 5155215

DOCUMENT-IDENTIFIER: US 5155215 A

**** See image for Certificate of Correction ****

TITLE: Polychelating agents for image and spectral enhancement (and spectral shift)

DATE-ISSUED: October 13, 1992

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|--------|-------|----------|---------|
| Ranney; David F. | Dallas | TX | | |

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TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging toolsAbstract Text (1):

A well logging system and method are disclosed for detecting the presence and estimating the quantity of gaseous and liquid hydrocarbons in the near wellbore zone. The system uses a gradient-based, multiple-frequency NMR logging tool to extract signal components characteristic for each type of hydrocarbons. To this end, new data acquisition methods are proposed in which measurements at different frequencies are interleaved to obtain, in a single logging pass, multiple data streams corresponding to different recovery times and/or diffusivity for the same spot in the formation. The resultant data streams are processed to determine mineralogy-independent water and hydrocarbon saturations and porosity estimates. Gas and oil saturations are used to obtain accurate estimates of the water content, permeability and other parameters of interest. In another aspect, a novel diffusion-enhanced data acquisition sequence is disclosed for use with low field gradient tools.

Brief Summary Text (2):

The present invention relates to nuclear magnetic resonance (NMR) logging and is directed more specifically to a system and method for detecting the presence and estimating the quantity of gaseous and liquid hydrocarbons in the near wellbore zone.

Brief Summary Text (3):

Petrophysical parameters of a geologic formation which are typically used to determine whether the formation will produce viable amounts of hydrocarbons include the formation porosity PHI, fluid saturation S, the volume of the formation, and its permeability K. Formation porosity is the pore volume per unit volume of formation; it is the fraction of the total volume of a sample that is occupied by pores or voids. The saturation S of a formation is the fraction of its pore volume occupied by the fluid of interest. Thus, water saturation $S_{sub.W}$ is the fraction of the pore volume which contains water. The water saturation of a formation can vary from 100% to a small value which cannot be displaced by oil, and is referred to as irreducible water saturation $S_{sub.Wirr}$. For practical purposes it can be assumed that the oil or hydrocarbon saturation of the formation $S_{sub.O}$ is equal to $S_{sub.O} = 1 - S_{sub.W}$. Obviously, if the formation's pore space is completely filled with water, that is if $S_{sub.W} = 1$, such a formation is of no interest for the purposes of an oil search. On the other hand, if the formation is at $S_{sub.Wirr}$ it will produce all hydrocarbons and no water. Finally, the permeability K of a formation is a measure of the ease with which fluids can flow through the formation, i.e., its producibility.

Brief Summary Text (4):

Nuclear magnetic resonance (NMR) logging is among the most important methods which have been developed to determine these and other parameters of interest for a geologic formation and clearly has the potential to become the measurement of choice for determining formation porosity. At least in part this is due to the fact that unlike nuclear porosity logs, the NMR measurement is environmentally safe and is unaffected by variations in matrix mineralogy. The NMR logging method is based on the observation that when an assembly of magnetic moments, such as those of hydrogen nuclei, are exposed to a static magnetic field they tend to align along the direction of the magnetic field, resulting in bulk magnetization. The rate at which equilibrium is established in such bulk magnetization upon provision of a static magnetic field is characterized by the parameter $T_{sub.1}$, known as the spin-lattice

relaxation time. Another related and frequently used NMR logging parameter is the so called spin-spin relaxation time constant T_{sub.2} (also known as transverse relaxation time) which is an expression of the relaxation due to non-homogeneities in the local magnetic field over the sensing volume of the logging tool.

Brief Summary Text (5):

Another measurement parameter used in NMR well logging is the formation diffusion D. Generally, diffusion refers to the motion of atoms in a gaseous or liquid state due to their thermal energy. The diffusion parameter D is dependent on the pore sizes of the formation and offers much promise as a separate permeability indicator. In an uniform magnetic field, diffusion has little effect on the decay rate of the measured NMR echoes. In a gradient magnetic field, however, diffusion causes atoms to move from their original positions to new ones, which moves also cause these atoms to acquire a different phase shifts compared to atoms that did not move, and will thus contribute to a faster rate of relaxation. Therefore, in a gradient magnetic field diffusion is a logging parameter which can provide independent information about the structure of the geologic formation of interest, the properties of the fluids in it, and their interaction.

Brief Summary Text (6):

It has been observed that the mechanisms which determine the values of T_{sub.1}, T_{sub.2} and D depend on the molecular dynamics of the sample being tested. In bulk volume liquids, typically found in large pores of the formation, molecular dynamics is a function of molecular size and inter-molecular interactions which are different for each fluid. Thus, water, gas and different types of oil each have different T_{sub.1}, T_{sub.2} and D values. On the other hand, molecular dynamics in a heterogeneous media, such as a porous solid which contains liquid in its pores, differs significantly from the dynamics of the bulk liquid and generally depends on the mechanism of interaction between the liquid and the pores of the solid media. It will thus be appreciated that a correct interpretation of the measurement parameters T_{sub.1}, T_{sub.2} and D can provide valuable information relating to the types of fluids involved, the structure of the formation and other well logging parameters of interest.

Brief Summary Text (7):

On the basis of the T_{sub.2} spectra, two specific methods for gas measurements are known in the prior art and will be considered briefly next to provide relevant background information. The first method is entitled "differential spectrum method" (DSM). The DSM is based on the observation that often light oil and natural gas exhibit distinctly separated T_{sub.2} measurements in the presence of a magnetic field gradient, even though they may have overlapping T_{sub.1} measurement values. Also, it has been observed that brine and water have distinctly different T_{sub.1} measurements, even though their D_{sub.0} values may overlap. The DSM makes use of these observations and is illustrated in FIG. 1 in a specific example for a sandstone reservoir containing brine, light oil and gas.

Brief Summary Text (8):

A second method known in the art is called "shifted spectrum method" (SSM). The SSM is illustrated in FIGS. 2A-B. Specifically, FIG. 2A shows synthetic T_{sub.2} decay curves in a gas bearing zone. The solid curve is for the short interecho time (.apprxq.0.6 msec) and the dashed curve corresponds to a longer interecho time of about 2.4 msec. FIG. 2B illustrates the T_{sub.2} spectra obtained from the inversion of the synthetic echo trains in FIG. 2A. The solid spectrum corresponds to the shorter interecho time, while the dashed spectrum line corresponds to the longer interecho time. In FIG. 2B the solid spectrum line corresponds to both brine and gas. The signal from gas is shifted out of the detectability range, so that the single spectrum peak is due to brine.

Brief Summary Text (9):

While prior art DSM and SSM methods provide a possible working approach to detection of gas using solely NMR data, the methods also have serious disadvantages which diminish their utility in practical applications. Specifically, typically two separate logging passes are required and therefore the methods show relatively poor depth matching properties on repeat runs. Furthermore, subtraction of signals from different logging passes is done in the T_{sub.2} spectrum domain which may result in losing valuable information in the transformation process, especially when the received signals have low signal-to-noise ratios (SNRs). In fact, for a typical logging pass, low hydrocarbon index (HI) of the gases in the formation, and relatively long T_{sub.1} times generally lead to low SNR of the received signals.

After transformation into the T.sub.2 spectrum domain even more information can be lost, thus reducing the accuracy of the desired parameter estimates.

Brief Summary Text (10):

In the parent application Ser. No. 08/822,567 filed Mar. 19, 1997, which is incorporated herein by reference for all purposes, a well logging system and method are disclosed for detecting the presence and estimating the quantity of gaseous and liquid hydrocarbons in the near wellbore zone. The approach presented in this application effectively addresses some of the concerns associated with prior art DSM and SSM methods. In particular, the proposed system uses a gradient-based, multiple-frequency NMR logging tool to extract signal components characteristic for each type of hydrocarbons. To this end, a data acquisition method is proposed in which measurements at different frequencies are interleaved to obtain, in a single logging pass, multiple data streams corresponding to different recovery times and/or diffusivity for the same spot in the formation. The resultant data streams are processed to determine mineralogy-independent water and hydrocarbon saturations and porosity estimates. Gas and oil saturations are used to obtain accurate estimates of the water content, permeability and other parameters of interest.

Brief Summary Text (11):

In most practical applications the approach used in the parent application is completely adequate and has been demonstrated to work. However, this approach relies on the presence of a static field gradient of typically 10-20 gauss/cm, and may not work well in an emerging class of wireline and LWD NMR logging tools that use lower field strengths, different field patterns and deeper depths of investigations (DOI).

Brief Summary Text (12):

Lower field gradients are important in achieving large sensitive volumes and the sensitivity required to perform deeper reading measurements. The combination of a lower field strength and deeper DOI's results in dramatically reduced static field gradients on the order of 0.3-3 gauss/cm. For the measurement method disclosed in the parent application, which employs variable wait times (1 sec to 12 sec) and fixed echo spacings (typ. 1 msec), it will generally be difficult to differentiate between the oil, water and gas phases in a weak gradient, because the method relies on differences in apparent T.sub.2 decay rates due to diffusion in a gradient field. One possible solution is to increase the echo spacing (i.e., from 1 msec to 10 msec), but such an approach would result in a significant loss of sensitivity because the sampling rate is only one-tenth of its original value. Therefore, it will be apparent that low-gradient logging tools require modified methods for successful gas/oil detection and quantification. -

Brief Summary Text (14):

In accordance with a preferred embodiment of the present invention a novel system and method are disclosed for the interpretation of NMR measurements of T.sub.1, D and effective T.sub.2 parameters made with a NMR logging tool using low field gradient magnetic fields. The present invention is based on a multi-frequency, gradient based logging tool providing the capability of conducting substantially simultaneous NMR measurements in adjacent non-overlapping resonant volumes of the geologic formation of interest. In particular, by hopping the resonant frequency of the device and thus sensing non-overlapping volumes of the formation, in accordance with a preferred embodiment of the present invention the time between experiments is reduced substantially without compromising the T.sub.1 relaxations or adopting imprecise T.sub.1 /T.sub.2 empirical relationships.

Brief Summary Text (15):

In one aspect, the present invention uses the multi-frequency capabilities of an NMR tool along with a data acquisition method suitable for the detection of gas on the basis of at least two sets of data points corresponding to a long (T.sub.RL) and short (T.sub.RS) recovery times, respectively. To this end, an interleaved pulse sequence is proposed in which at least two CPMG pulses associated with a first resonant frequency are followed by at least two CPMG pulses associated with a second resonant frequency. Due to the fact that each resonant frequency excites protons in a separate volume of the formation, pairs of complex data points can be collected at substantially the same depth mark, such that the first data point corresponds to a short recovery time T.sub.RS while the second data point corresponds to a long recovery time T.sub.RL.

Brief Summary Text (16):

In accordance with a preferred embodiment of the present invention, the sequence of data pairs is used next to form two complex time-domain signal vectors x and y corresponding to the long and the short recovery times, respectively. Following calibration, a difference and a sum signal vectors $(x-y)$ and $(x+y)$ are formed. The difference signal is phase corrected to obtain a real-time signal using phase information from the sum signal. Next, matched filters corresponding to a gas phase and an oil phase are computed, in real time, using information about reservoir temperature, pressure and other known probe and/or formation properties. The phase-corrected difference signal is then filtered using the matched filters to separate oil and gas signal components from the input NMR signals. The output signals from the matched filters are next used to obtain gas- and oil-porosity estimates and further to reconstruct the oil and gas components in the original measurement signals. The reconstructed components are subtracted from the sum signal $1/2(x+y)$ to provide only the brine component of the original signal. This brine component is finally subjected to $T_{sub.2}$ inversion to obtain an estimate of the irreducible water saturation and water porosity. To further increase the separation between different hydrocarbon phases in the formation, diffusion-weighted measurements can also be used according to the SSM approach.

Brief Summary Text (17):

The system and method in accordance with the present invention have been shown to be very sensitive due to the fact that the gas and oil components of the original signal are determined from the original signals, prior to $T_{sub.2}$ spectrum inversion. The method of the present invention has been demonstrated to give more accurate parameter estimates than other presently available NMR logging techniques and can be used advantageously in low-porosity formations, where low signal-to-noise ratios (SNRs) tend to broaden all $T_{sub.2}$ components. Additionally, corrections for hydrogen index (HI) and incomplete longitudinal recovery are also provided to calculate estimates of gas-filled porosity and to correct both apparent NMR porosity (MPHI) and free fluid index FFI, which are necessary to obtain accurate estimates of formation permeability.

Brief Summary Text (18):

In another aspect, the present invention is based on the use of a modified CPMG (Carr-Purcell-Meiboom-Gill) sequence that is characterized by two echo spacings. The first echo is subject to a variable echo spacing TD; ranging from approximately 1 ms to hundreds of milliseconds. With such a large possible range for the echo spacing TD, the diffusion characteristics of the fluid(s) involved can be made a dominant factor for amplitude decay. In a preferred embodiment, the second and all following echoes are generated with short spacings (TE, typically 1 msec). In this period, the influence of diffusion is negligible in a low field gradient, and a dense sampling regime is maintained, resulting in good sensitivity. The amount of amplitude loss incurred in the TD interval is directly related to the diffusivity of the hydrogen-bearing fluids. In a preferred embodiment, TD is a parameter that varies from a low of TE (i.e., the case in which the modified sequence reduces to a simple CPMG sequence) to highs of hundreds of milliseconds.

Drawing Description Text (3):

FIG. 1 is an illustration of the differential spectrum method for identifying the presence of gaseous components.

Drawing Description Text (4):

FIG. 2A illustrates synthetic $T_{sub.2}$ decay curves used in the Shifted Spectrum method. FIG. 2B shows $T_{sub.2}$ spectra obtained from inversion of the synthetic echo trains in FIG. 2A.

Drawing Description Text (7):

FIG. 5A shows the hydrogen index (HI) of methane as a function of depth at temperature gradients of 1, 1.5 and 2.degree. F./100 ft.

Drawing Description Text (8):

FIG. 5B shows the dependency of the longitudinal relaxation time $T_{sub.1}$ as a function of depth at temperature gradients of 1, 1.5 and 2.degree. F./100 ft, and pressure gradient of 43.3 psi/100 ft.

Drawing Description Text (10):

FIG. 5D shows the apparent transverse relaxation time $T_{sub.2}^*$ based on diffusivity $D_{sub.0}$ as in FIG. 5C, diffusion restriction $D/D_{sub.0}$, and magnetic field temperature gradient of -0.18%/degree.C.

Drawing Description Text (11):

FIG. 5E shows values for the T.sub.1 parameter of methane gas and light oils as a function of logging depth.

Drawing Description Text (12):

FIG. 5F illustrates the self diffusion coefficients D.sub.0 for methane, water and light oil as a function of logging depth.

Drawing Description Text (13):

FIG. 5G illustrates the measured T.sub.2R for gas and oil as a function of logging depth.

Drawing Description Text (14):

FIG. 6 is an illustration of an interleaved data acquisition pulse sequence for T.sub.1 weighted and diffusion-weighted saturation recovery CPMG echo trains in a specific embodiment of the present invention using two tool frequencies.

Drawing Description Text (17):

FIG. 9A shows sample response of the gas and the oil matched filters in accordance with the present invention; FIG. 9B is the magnitude of the Fourier transform of the matched filter responses shown in FIG. 9A.

Drawing Description Text (18):

FIG. 10 shows orthogonalized filter functions of the gas and the oil matched filters in accordance with the present invention.

Drawing Description Text (20):

FIGS. 12A-C illustrate a modified pulse sequence used in accordance with the present invention for low field gradient magnetic tools. FIG. 12A illustrates the case in which the modified sequence reduces to a CPMG pulse sequence with a single echo spacing. FIGS. 12B and 12C illustrate pulse sequences with increased diffusion time TD.

Drawing Description Text (21):

FIGS. 13A, 13B 14A and 14B illustrate simulation results showing computed echo amplitudes for the case of no diffusion and signal attenuation due to diffusion.

Detailed Description Text (2):

During the course of the description like numbers will be used to identify like elements shown in the figures. Bold face letters represent vectors, while vector elements and scalar coefficients are shown in standard print.

Detailed Description Text (4):

In order to separate signal contributions from different fluids, an NMR tool must be able to operate in a three-dimensional parameter space: T.sub.2 (transverse decay time), measured by a CPMG pulse-echo sequence; T.sub.1 (longitudinal polarization time), measured by variable saturation-recovery times; and D (apparent, restricted diffusivity), measured by varying the CPMG pulse-echo spacing τ . in the presence of a magnetic field gradient.

Detailed Description Text (5):

In a preferred embodiment of the present invention these measurements in a moving logging tool are enabled using the system illustrated schematically in FIGS. 3(A-C). In particular, FIG. 3A illustrates, in relatively general form, apparatus for carrying out NMR borehole diffusion coefficient determinations in accordance with a preferred embodiment of the present invention. The apparatus includes a first portion 106, which is arranged to be lowered into a borehole 107 in order to examine the nature of materials in the vicinity of the borehole.

Detailed Description Text (10):

The complex time-domain signal from the RF receiver preamplifier 126 is supplied to an RF receiver 40 which optionally receives input from a phase shifter 44. Phase shifter 44 receives an input from variable frequency RF source 36. As discussed in more detail next, in a preferred embodiment of the present invention phase correction is done using signal processing algorithms instead. Receiver 40 outputs via an A/D converter with a buffer 46 to computer 50 for providing desired well logging output data for further use and analysis. Pulse programmer 146 controls the gradient coil power supply 129 enabling and disabling the flow of current, and hence

the generation of static or pulsed field gradients, according to the commands of the computer 50. Some or all of the elements described hereinabove as being disposed in an above-ground housing, may instead be disposed below ground. Improved devices and measurement methods which can be used for the probe 106 are described generally in U.S. Pat. Nos. 4,710,713; 4,717,876; 4,717,877; 4,717,878, 5,212,447; 5,280,243; 5,309,098 and 5,412,320 all of which are commonly owned by the assignee of the present invention. A specific embodiment of the tool which can be used in accordance with the present invention is also discussed in detail in Chandler et al., "Improved Log Quality with a Dual-Frequency Pulsed NMR Tool," paper SPE 28365, presented at the 69-th Annual Technical Conference and Exhibition, Society of Petroleum Engineers, New Orleans, Sep. 25-28, 1994. The contents of these patents and the Chandler et al. paper are hereby expressly incorporated for all purposes.

Detailed Description Text (11):

FIG. 3B is a block diagram of the system in accordance with a specific embodiment of the present invention which shows individual block components for controlling data collection, processing of the collected data and displaying the measurement results. In FIG. 3B the MRI electronics 30 comprises an MRI probe controller and pulse echo detection electronics. The output signal from the detection electronics is processed by data processor 52 to analyze the relaxation characteristics of the sample. The output of the data processor 52 which in accordance with a preferred embodiment of the present invention comprises at least two complex time-domain data sets is provided to the parameter estimator 54. Measurement cycle controller 55 provides an appropriate control signal to the MRI probe. The processed data from the log measurement is stored in data storage 56. Data processor 52 is connected to display 58 which is capable of providing a graphical display of one or more measurement parameters, preferably superimposed on display data from data storage 56. The components of the system of the present invention shown in FIG. 3B can be implemented in hardware or software, or any combination thereof suitable for practical purposes.

Detailed Description Text (13):

Specifically, in a preferred embodiment the system of the present is capable of "hopping" from one operating frequency to another, the effect of which is to shift the radial position of the resonant volume for the tool. The frequency shift is selected in such manner that at least two non-overlapping resonant volumes are formed; each new resonant volume associated with a different frequency being filled with fully relaxed protons. Hopping between two or more (i.e., K) frequencies thus allows reducing the time between experiments approximately by a factor of K, without compromising complete T_{sub.1} measurements or adopting imprecise empirical T_{sub.1}/T_{sub.2} relationships; the logging speed for the tool can accordingly be increased approximately K times. This feature is illustrated in FIG. 3C in which hopping between two different frequencies is shown to result in conducting measurements in two non-overlapping resonant volumes. In the specific example illustrated in FIG. 3C each frequency band is about 6 kHz wide and the two mean band frequencies are offset by about 15 kHz. This mode of operation forms two concentric annuli, each 0.04 inch (0.1 cm) thick, separated center to center by about 0.09 inches (0.23 cm).

Detailed Description Text (15):

The MRIL tool used in a preferred embodiment of the present invention generally has a vertical excitation/response function that can be represented by a near-perfect rectangular aperture. In a specific embodiment, a high vertical resolution, 24" (60.96 cm) long aperture, or a lower vertical resolution, 43" (109.22 cm) long, aperture are used. In order to perform T_{sub.1} -weighted signal measurements, as discussed in detail below, it is required that the formation volume being sensed remains substantially unchanged over the course of a recovery period. Specifically, for a moving tool, it has been determined that volume changes of about 10-20% still provide adequate measurement accuracy. This condition is illustrated in FIG. 4 which shows the relationships between saturation-recovery time interval T_{sub.R}, logging speed v and aperture length L. Using the notations in FIG. 4, it is possible to impose either a minimum aperture length or a maximum tool logging speed requirement which must satisfy the condition for substantial measurement stationarity. For example, in the specific embodiment of a 24" long aperture, assuming recovery time T_{sub.R} = 2 s, and imposing a 10% accuracy requirement, it can be seen that the maximum allowed tool speed is $v = 5 \times 2.4^2 / 2 \text{ s} = 6 \text{ ft/min}$ (3.05 cm/sec). For the alternate configuration using a 43" long antenna, under the same assumptions the maximum tool speed is about 11 ft/min (5.588 cm/sec).

Detailed Description Text (16):

In accordance with the present invention, for the purposes of making T.sub.1 weighted measurements with a moving logging tool at least one long saturation-recovery (SR) interval is required, preferably of about 8-10 sec. It should be noted that for such an interval logging data is substantially insensitive to vertical tool displacement because at the end of the interval the formation magnetization is already close to an equilibrium. The transverse magnetization left after a CPMG sequence is quickly dephased in the strong gradient field. At this point, a saturation-recovery (SR) measurement can be started, as known in the art. The recovered magnetization is read out by the next CPMG train.

Detailed Description Text (18):

Random lateral tool motion is a source of concern for the validity of the downhole T.sub.1 weighted measurements in accordance with the present invention. The reason is that since the sensitive volume for the tool resembles a cylindrical slice of about 1-2 mm thickness, lateral swaying of the tool could cause an influx of fully polarized magnetization and thus give incorrect measurements. Studies of actual log data repeatedly acquired over the same zones, however, show monotonic recovery behavior of sequences with increasing SR intervals, indicating that lateral tool motion generally has a negligible effect on the actual measurements. Further evidence that side effects due to lateral motion of the tool are insignificant is provided by the consistency of MPHI and FFI measurements made with the tool, which are both independent of the T.sub.1 parameter.

Detailed Description Text (19):

Another source of concern in NMR logging is the relatively shallow depth-of-investigation which, due to the generally cylindrical shape of the resonance volume of the tool, also depends on the borehole size. Thus, in some cases shallow depth-of-investigation along with the fact that invading fluid in the borehole replaces gas can lead to a reduction in the gas effect which can be sensed by the tool. It should be noted, however, that the MRIL tool's sensitive volume has an approximately 4" (10.16 cm) blind zone extending from the borehole wall. The presence of such blind zone effectively limits the influence of fluid invasion. Experimentally, in most cases residual hydrocarbon saturations seen by the tool have been shown to be sufficient for hydrocarbon detection purposes and can be close to uninvaded saturations.

Detailed Description Text (20):

The CPMG pulse sequences used with the MRIL tool in accordance with the present invention have been described generally in U.S. Pat. No. 5,212,447 assigned to the assignee of the present application. Also discussed in this patent are specific methods of conducting NMR measurements, including derivations of the diffusion coefficient D and/or T.sub.2. The relevant portions of the disclosure of the U.S. Pat. No. 5,212,447 are expressly incorporated herein for all purposes. The MRIL tool used in accordance with a preferred embodiment of the present invention stores multiple pulse sequences downhole, in a memory (not shown in FIGS. 3A and B) within probe 106. These sequences are then activated by commands from the measurement time controller 55 of the surface system. At the surface, raw tool data are separated into data streams and associated with the correct calibration and correction tables in data processor 52. An essentially unlimited number of pulse sequences can be used quasi-simultaneously, as described in more detail next. In an alternative preferred embodiment of the present invention the operation of the tool can be re-programmed on command from surface controller 55.

Detailed Description Text (21):

In accordance with another aspect of the invention, LWD NMR logging tools are desirable that use lower field strengths, different field patterns and deeper depths of investigations (DOI). An example of such a tool is disclosed in European Patent Application 99200567.8 (Document EP 0 940 688 A2) entitled "NMR logging-while drilling tool generating an axisymmetric magnetic field having straight contour lines in the resonance region." Another example is provided by the basic magnet configuration described in U.S. Pat. No. 4,629,986. The above references are incorporated herein by reference for all purposes.

Detailed Description Text (23):

In accordance with a preferred embodiment of the present invention several parameters which correspond to the gas and the oil phases of the formation are computed in real time. Due to the fact that logging conditions dynamically change during the course of a pass, correction for various factors which may affect the accuracy of the measurements have to be made. In the following paragraphs, a brief

discussion is presented on the specifics of the parameter computations and the required corrections used in accordance with a preferred embodiment of the present invention to estimate the relative quantities of gas and oil in a formation of interest.

Detailed Description Text (25):

It is known in the art that the static field gradient required for downhole diffusion measurements induces stimulated echo effects within a CPMG echo train. These stimulated echoes partially undergo $T_{sub.1}$ relaxation and therefore benefit less from the re-focusing effects of repeated π pulses in a standard CPMG sequence. In accordance with a preferred embodiment of the present invention this problem can be treated by introducing the concept of "effective" relaxation times, as described in more detail next.

Detailed Description Text (26):

In particular, it is known that the classic Carr-Purcell expression for spin echo attenuation due to transverse relaxation and diffusion in a field gradient which, using the standard notations above, is given by the expression: ##EQU1##

Detailed Description Text (27):

strictly speaking is valid only if: (a) the gradient G is small, or (b) if only the on-resonance portion of the spin spectrum is utilized. As indicated above, however, the MRIL tool operates with a relatively strong gradient field, on the order of about 15-25 G/cm. In addition, low signal-to-noise considerations make it necessary to utilize the full bandwidth of the tool, so that strong off-resonance effects are necessarily included in the echo signals. Thus, for example, even for the simplest $T_{sub.2}/D$ experiment which requires at least two different pulse-echo spacings τ , a correction in the expression in Eq. (1) is required in order to avoid systematic errors. Consequently, the observed echo decay signal has to be modeled as a complex superposition of longitudinal relaxation, transverse relaxation and different diffusion times.

Detailed Description Text (28):

Therefore, in accordance with the present invention, the signal observed at the N -th echo is modeled as a superposition of all possible combinations of transitions between transverse and longitudinal magnetization and is given by the expression: ##EQU2##

Detailed Description Text (29):

Using the expression in Eq. (2), the effect of diffusion dephasing is taken into account by introducing "effective" transverse relaxation times $T_{sub.1.sup.} \cdot \dagger$ and $T_{sub.2.sup.} \cdot \dagger$, given by the following expressions:

Detailed Description Text (30):

It can be shown that direct echoes ($i=N$) decay with a rate $1/T_{sub.2.sup.} \cdot \dagger$; indirect echo decay ($i < N$) is controlled by $1/T_{sub.1.sup.} \cdot \dagger$ and by $1/T_{sub.2.sup.} \cdot \dagger$. Without diffusion, indirect echoes decay either slower or at the same rate as direct echoes. With very fast diffusion, however, indirect echoes drop out faster than direct ones. The effect on combined echo amplitudes primarily depends on the receiver's bandwidth and has been determined to require an about 15% correction at high diffusion rates.

Detailed Description Text (31):

It should be noted that the expressions for the effective relaxation rates in Eq. (3) refer to the echo decay process, and not to the recovery of longitudinal magnetization, which is controlled by $T_{sub.1}$. For gases, both effective relaxation times are dominated by the diffusion term in a gradient field and therefore $T_{sub.1} >> T_{sub.1.sup.} \cdot \dagger \approx T_{sub.2.sup.} \cdot \dagger / 3$. In this case, the echo train decays slightly faster than expected, and an analysis based on the standard Carr-Purcell formula will overestimate the diffusion parameter D . This problem is corrected by inserting into the Carr-Purcell formula of an effective pulse-echo spacing $\tau_{sub. eff}$, which incorporates the influence of both pulse width and receiver bandwidth:

Detailed Description Text (34):

As evident from Eq. (4), the prediction of $T_{sub.2.sup.} \cdot \dagger$ in the gas phase generally requires knowledge of the field gradient G , which is dependent on the probe temperature. A specific example of measurements of the depth-of-investigation (diameter of the sensitive zone) and the magnetic field gradient values, as

functions of probe temperature, are summarized in Table 1.

Detailed Description Text (35):

Typical values used in Eq. (4) are $\tau_{eff} = 0.65$ ms, $\tau = 26750$ s.⁻¹ G.⁻¹, and $G = 18$ G/cm. Probe temperature, as reported by a sensor embedded in the permanent magnet of the MRIL tool, is always recorded, which allows the calculation of the field gradient G at any point on the log.

Detailed Description Text (36):

3) Parameterization of H_I , $T_{sub.1}$ and $T_{sub.2}$

Detailed Description Text (37):

The matched filter signal processing method of the present invention, described in more detail below, requires the calculation of hydrocarbon (oil and gas) signatures. These components are assumed to be the non-wetting phase, i.e., to be generally characterized by their bulk relaxation properties. As known in the art, the effects of temperature and pressure on $T_{sub.1}$ and D of the gas phase substantially cancel each other, resulting in fairly stable and predictable values for both parameters, for which mathematical expressions are available. On the other hand, the corresponding values for the oil phase are generally dependent on the formation and are determined in accordance with the present invention from sample measurements conducted prior to the logging experiment.

Detailed Description Text (38):

In particular, the hydrogen index (H_I) of oil is assumed to be 1.0. The measured drop in NMR porosity is typically observed in gas zones, because $H_{I,sub.g} < 1$. Most natural gases are predominantly methane. FIG. 5A shows $H_{I,sub.g}$ variations between about 0.2 and 0.6 for a methane gas under typical conditions. In overpressured reservoirs $H_{I,sub.g}$ can be about 0.7. Accordingly, the gas H_I is sufficient to give readily detectable signals from gas. For methane gas, in accordance with a preferred embodiment of the present invention the corresponding index $H_{I,sub.g}$ is estimated mathematically using the expression $2.25 \cdot \rho$, where ρ is the gas density in g/cm.³, calculated by solving the equation of state. For gases other than methane, or for mixed gases, the multiplying factor is less than 2.25. For example, for a typical gas mix, characterized as $C_{sub.1.1} H_{sub.4.2}$, the factor becomes 2.17. In an alternative preferred embodiment of the present invention, the hydrogen index of different hydrocarbons can also be estimated using the expressions presented, for example, in "Schlumberger: Log Interpretation Principles/Applications," Schlumberger Educational Services, 1989, pp. 5-20 and 5-21, the content of which is expressly incorporated herein.

Detailed Description Text (39):

A simple power law has been found sufficient to fit published laboratory data for longitudinal relaxation time $T_{sub.1}$ of methane gas, as well as log data. The expression used in accordance with the present invention is:

Detailed Description Text (40):

where $T_{sub.1}$ is measured in seconds, the density ρ in g/cm.³ and the absolute temperature T is in degrees Kelvin. Eq. (5) is valid for gas densities up to about 0.3 g/cm.³; higher densities generally approaching a liquefied gas state.

Detailed Description Text (41):

In accordance with the present invention the non-wetting oil phase relaxes with its bulk relaxation $T_{sub.1,o}$, which is determined, for example, by using viscosity measurements of a sample. It has been determined that in order to successfully detect liquid hydrocarbons, for the $T_{sub.1}$ -weighted measurements in accordance with the present invention a long $T_{sub.1}$ component (low viscosity) on the order of 1-2 s is necessary. The relatively large values for the parameter $T_{sub.1}$ of light hydrocarbons provide a mechanism for distinguishing these fluids from water, since $T_{sub.1}$ of water in rocks is almost always less than about 500 msec. In partially hydrocarbon-saturated water wet rock the hydrocarbon-water contrast is even better because $T_{sub.1}$ (and $T_{sub.2}$) of water are shorter, due to the fact that water typically resides in the smallest pores.

Detailed Description Text (42):

FIG. 5E shows, on the other hand, values for the $T_{sub.1}$ parameter of gas (methane) and light oils at depths below 4000 feet. Both curves were computed assuming a geothermal gradient of 1.5.degree. F./100 feet. The oil curve was computed assuming

a temperature-dependent viscosity, using the expression $\eta = \eta_0 \exp(Q/RT)$, where $\eta_0 = 0.01$ cp, $Q = 10.5$ kJ/mol and $R = 8.314$ J/mol/K. As seen in the figure, due to different relaxation mechanisms, $T_{2\rho}$ for methane can be relatively short, i.e., between about 2.5 and 4 seconds, while in the specific example $T_{2\rho}$ for oil can be very long (on the order of 10 sec). Standard logging practice requires to set the wait time between successive CPMG pulse trains long enough for substantially full recovery (about 95%) of the longitudinal magnetization. Accordingly, waiting times for a particular measurement have to be adjusted dependent on the specific oil.

Detailed Description Text (43):

The apparent diffusivity D of a fluid depends both on the self-diffusion coefficient D_0 and the restrictions imposed by the pore space. In accordance with a preferred embodiment of the present invention, an experimental temperature and density relationship for unrestricted gas diffusion D_0 is used, which can be expressed mathematically as:

Detailed Description Text (44):

where D_0 is measured in cm^2/s , the temperature T is measured in degrees Kelvin and the density ρ is expressed in g/cm^3 . Below 7,000 ft, the opposing effects of temperature and pressure stabilize the diffusion parameter D_0 at a value of about $10^{-3} \text{ cm}^2/\text{s}$. Diffusion restriction in the pore space should also be taken into account since the diffusion length (given by $\sqrt{2\tau D_0}$) is approximately equal to 10 μm . D/D_0 ratios in rock samples at this length scale have been observed ranging from about 0.55 (Indiana limestone) to about 0.9 (oolitic limestone). Sandstone samples have been found to cluster in a tight D/D_0 ratio range of 0.7-0.8, which is consistent with experimental observations of $T_{2\rho}$ from log data.

Detailed Description Text (45):

Because of diffusion, the intrinsic relaxation rate $1/T_{2\rho}$ for gas is negligible compared to $1/T_{2\rho}$. (see Eq. (3)). Similarly, the diffusivity of the oil phase is small compared to that of the gas phase. Consequently, the parameters $T_{2\rho}$ and $T_{2\rho}$, which are used in the matched filter expression considered next are much larger than both $T_{2\rho}$ and also much larger than the total acquisition time required to separate oil from gas signals. As indicated above, numerical values for these parameters can be obtained, for example, from sample measurements.

Detailed Description Text (46):

FIG. 5F illustrates the self diffusion coefficients D_0 for methane, water and light oil. All curves are based on geothermal gradient of 1.5 degree F./100 feet, and (for gas) a hydrostatic pressure gradient. As seen, the methane D_0 is at least about 50 times larger than that of water and light oil. The resulting contrasts in the measured $T_{2\rho}$ (i.e., $T_{2\rho}$) for gas compared to oil are shown in FIG. 5G. The plots include the effect of temperature and pressure on $T_{2\rho}$ (see FIG. 5E) and D (see FIG. 5F) for both fluids and the effect of temperature on the parameter G for the tool. Moderate restriction diffusion effect on gas and no restriction effects on oil diffusion was assumed, i.e., $(D/D_0)_{\text{gas}} = 0.7$; $(D/D_0)_{\text{oil}} = 1$. Comparison of FIGS. 5E and 5G reveals that gas has a high ratio $T_{2\rho}/T_{2\rho}$ (larger than about 200) at all depths, which is a characteristic signature of gas. For light oil, however, this ratio is approximately equal to one and rises slowly with increased depth.

Detailed Description Text (47):

Table 2 summarizes expressions for the parameter estimates of different fluids used in accordance with a preferred embodiment of the present invention.

Detailed Description Text (48):

For illustrative purposes, examples of pre-calculated values for H_1 , diffusivity and the relaxation time parameters $T_{2\rho}$ and $T_{2\rho}$ as functions of depth are shown in FIGS. 5A to 5D. In particular, FIG. 5A shows the hydrogen index (HI) of methane as a function of depth at different temperature gradients; FIG. 5B shows the dependency of the longitudinal relaxation time $T_{2\rho}$ as a function of depth at temperature gradients of 1, 1.5 and 2 degree F./100 ft, and pressure gradient of 43.3 psi/100 ft; FIG. 5C shows the dependency of the self-diffusion coefficient D_0 of methane as a function of depth; and FIG. 5D shows the apparent transverse relaxation time $T_{2\rho}$ based on diffusivity D_0 as in FIG. 5C, diffusion restriction D/D_0 , and magnetic field

temperature gradient of $-0.18\%/^{\circ}\text{C}$.

Detailed Description Text (51):

As indicated above, the MRIL tool of the present invention is capable of performing separate, quasi-simultaneous measurements in different sensitive volumes by simply switching the operating frequency of the tool by a small amount. In accordance with a preferred embodiment of the present invention, this multi-frequency capability of the MRIL tool is used to provide a new data acquisition method which is particularly suitable for the detection of gas on the basis of NMR measurements with different recovery times $T_{\text{sub.Ri}}$. To this end, with reference to FIG. 6, a novel interleaved pulse sequence is proposed in which at least two CPMG pulses 210 and 220 associated with resonant frequency $F_{\text{sub.2}}$ are followed by at least two CPMG pulses 230, 240 associated with a different resonant frequency $F_{\text{sub.1}}$. As shown in FIG. 6, the NMR measurement is continued next using at least two new pulses 250, 260 at the initial resonance frequency $F_{\text{sub.2}}$, followed by at least two separate pulses 270, 280 at the $F_{\text{sub.1}}$ frequency. Due to the fact that resonant frequency $F_{\text{sub.1}}$ excites protons only in volume 1 of the formation and resonant frequency $F_{\text{sub.2}}$ excites protons only in volume 2 of the formation, pairs 225, 245, 265, etc., of independent complex data points can be collected at each depth mark. As shown for illustrative purposes in FIG. 6, the first data point in each pair, generally designated as $B_{\text{sub.i}}$ corresponds to a short recovery time $T_{\text{sub.R1}}$, while the second data point, generally designated as $A_{\text{sub.i}}$, corresponds to a long recovery time $T_{\text{sub.R2}}$.

Detailed Description Text (52):

Thus, using the data acquisition sequence illustrated in FIG. 6, by "hopping" the resonance frequency $F_{\text{sub.i}}$ of the tool, and alternating between adjacent resonant volumes of the formation one can obtain a sequence of signal pairs, each pair corresponding to substantially the same depth mark in the formation, but measured at different recovery times. It should further be noted that data for two different recovery times need not necessarily be obtained from only two different frequencies. For example, two or more measurements associated with different frequencies can be combined (i.e., averaged) to result in a single data stream corresponding to either a short, or a long recovery time. Furthermore, it should be clear that by using more than two resonance frequencies, and applying a correspondingly larger number of pulses in each resonant volume, the data acquisition method of the present invention can easily be extended to the more general case of M-tuple measurement data sets, each measurement point corresponding to a different recovery time $T_{\text{sub.Ri}}$.

Detailed Description Text (54):

The data acquisition method was described above with reference to identical CPMG sequences, which mode is referred to in the present application as $T_{\text{sub.1}}$ -weighted acquisition. Data from this acquisition mode is suitable for the Differential Spectrum Method (DSM) described in the Akkurt et al. paper. Notably, however, the method is also suitable for direct signal subtraction in the time domain, as described in more detail next.

Detailed Description Text (55):

In an alternative preferred embodiment of the present invention, a novel data acquisition mode referred to as $T_{\text{sub.1}}$ - and diffusion-weighted acquisition can also be used. As indicated above with reference to the SSM method, the contrast between liquid and gas signals can be enhanced by using a slightly larger pulse-echo spacing for the CPMG train associated with the shorter recovery interval. This embodiment is illustrated in FIG. 6 using two different intervals $\tau_{\text{sub.i}}$ for each successive pulse in the same resonance volume. It has been found, however, that it is not necessary to eliminate the gas signal altogether. For example, an increase by only 40% in the pulse echo τ has been found to cause a 50% decrease in the diffusion-induced part of $T_{\text{sub.2}}$. As indicated above with reference to the SSM method, because of diffusion dominance, the effect is much more pronounced for gases than for liquids, and can accordingly be used to enhance the separation of the two phases.

Detailed Description Text (56):

In another aspect of the invention, a modified pulse sequence is disclosed preferably for use with low field gradient tool measurements. The key idea is to use a modified CPMG (Carr-Purcell-Meiboom-Gill) sequence that is characterized by two echo spacings. The first echo is subject to a variable echo spacing TD ; ranging from approximately 1 ms to hundreds of milliseconds. With such a large range possible for TD , the diffusion characteristics of the fluid(s) involved can be made a dominant factor for amplitude decay. The second and all following echoes are generated with

short spacings (TE, typically 1 msec). In this period, the influence of diffusion is negligible in a low field gradient, and a dense sampling regime is maintained, resulting in good sensitivity. The amount of amplitude loss incurred in the TD interval is directly related to the diffusivity of the hydrogen-bearing fluids. TD is a parameter that varies from a low of TE (i.e. a simple CPMG sequence) to highs of hundreds of milliseconds.

Detailed Description Text (57):

An example of the sequence used in a preferred embodiment is shown in FIGS. 12A-C. In particular, FIG. 12A illustrates the trivial case of $TD=TE$, which is a standard CPMG sequence used as a reference. The TE interval is chosen short enough, such that the influence of diffusion on the echo amplitude decay is negligible. As shown in FIGS. 12B and 12C, in accordance with this aspect of the invention the TD interval is increased in successive measurements. In a preferred embodiment, the granularity of the TD interval is chosen such that the later echoes line up in time with those of the CPMG scan and a one-to-one correspondence can be established. In a preferred embodiment, the second TD value can be chosen to attenuate or eliminate signals from the gas phase only. The difference between corresponding echoes (as shown in FIGS. 12A and 12B) would therefore be signal corresponding to the presence of gas. In accordance with the preferred embodiment the third TD value can be selected to attenuate or eliminate both gas and free water signals. Accordingly, the remaining signal (illustrated in FIG. 12C) could come only from the oil phase, which typically has the slowest self-diffusion rate.

Detailed Description Text (60):

where A is the echo amplitude, γ is the gyromagnetic ratio, G is the field gradient, Tx is the interval TD or TE, respectively, and D is the self-diffusion constant. For the purpose of this discussion, spin-lattice and spin-spin relaxation are ignored for the moment. To illustrate the method, the following values can be used:

Detailed Description Text (61):

It will be appreciated that other values can be selected in different applications. With the above assumptions, in the TE interval and in the case $TD=TE$, even for the fastest diffusion case, the diffusion-induced signal decay rate is only:

Detailed Description Text (62):

which is small compared to typical intrinsic $T_{2\text{sub}}$ rates (.about.0.25 sec.^{sup.}-1) and typical pulse-echo train lengths (.about.1 sec). Therefore, in accordance with this aspect of the invention during the TE interval the influence of diffusion can be ignored. Further, it will be appreciated that the case $TD=TE$ can serve as a reference without echo attenuation due to diffusion.

Detailed Description Text (63):

In accordance with the present invention, the next TD value should attenuate the gas signal by approximately 86% (i.e., two time constants). It follows that TD should obey the following equation:

Detailed Description Text (65):

The amplitude of the free-water signal is attenuated by a factor of

Detailed Description Text (66):

The echo train with $TD=32$ ms contains 14% of the gas signal, 82% of the free-water signal and 98% of the oil signal (from an analogous calculation). An echo-by-echo subtraction from the $TD=1$ ms train isolates the gas signal as follows: 86% gas signal, 18% free-water signal and 2% oil signal. The bound-water signal is eliminated by considering only echoes that occur after 32 ms.

Detailed Description Text (67):

For the current example, a third TD value is chosen equal to 70 ms to isolate the oil signal. In this case, the gas signal is completely eliminated, the free-water signal is attenuated by 86% and the oil signal remains at 82% of its value.

Detailed Description Text (69):

It will be appreciated that the above values are used as guidelines only and can be replaced in practical application using the described computation techniques.

Detailed Description Text (71):

In a first aspect, the method for fluid detection in accordance with a preferred embodiment of the present invention assumes data acquisition in the presence of a

static magnetic field gradient in the range 10-30 G/cm. The method further requires at least two separate measurements with different saturation-recovery times $T_{sub.Ri}$ and/or different echo-to-echo spacings, and is implemented using the data acquisition sequence illustrated in FIG. 6. In addition, the very low signal-to-noise (SNR) levels which are due to HI losses and incomplete magnetization recovery in a typical NMR measurement necessitate signal detection using two-channel complex data stream. Therefore, in a preferred embodiment of the present invention data is acquired in two orthogonal channels, and averaged over a vertical logging interval to increase the SNR for the acquired measurement data.

Detailed Description Text (72):

Turning next to FIG. 7, it shows in semi-block diagram form the signal processing method in accordance with a preferred embodiment of the present invention. Specifically, the determination of water, oil and gas saturations in the sensitive volume begins by performing at least two interleaved $T_{sub.R1}$ -weighted measurements to separate the wetting phase (brine, surface-dominated relaxation) from the non-wetting phase (light hydrocarbons, bulk-dominated relaxation). Optionally, these measurements can be diffusion-weighted as well. As shown in FIG. 7, this results in two parallel data sets of complex time-domain data. Data sequence 310 generally corresponds to data obtained from the long recovery time $T_{sub.R2}$, while data sequence 320 corresponds to data obtained from the short recovery time $T_{sub.R1}$. Between about 150 and 300 data points are used in each sequence. Preferably, the recovery times used are about 2 sec for $T_{sub.R1}$ and about 8 sec for $T_{sub.R2}$. Pairs of echo trains are formed by matching overlapping short and long TR intervals thereby minimizing the systematic variations introduced when formation bed boundaries are crossed.

Detailed Description Text (73):

Following the data acquisition process, in block 325 the two data sets are corrected using calibration data from blocks 315. Specifically, such calibration data is obtained from samples at room temperature, with 100% water saturation, for example in a water-filled tank. FIG. 8A shows two such calibrated data sequences as functions of time. As shown in FIG. 8A, the magnitude values for the measurement signals are conveniently calibrated in porosity units (p.u.). Skipping for a moment block 330, next the complex difference between the signals in each data pair is obtained in subtractor 335 to eliminate the brine contribution; the sum signal is obtained in adder 340 to estimate the input signal phase and phase-correct the difference signal in block 335 accordingly. Specifically, it has been observed that while the absolute phase of the NMR signal is subject to slow variations due to hole and tool conditions, it shows excellent short-term stability. Therefore, the phases of the sum and the difference signals are approximately equal. In accordance with the present invention this feature is used to correct the phase of the difference signal on the basis of a phase estimate for the sum signal which was found to be comparatively more accurate.

Detailed Description Text (74):

In particular, a depth-averaged signal phase is computed in block 350 from the complex sum signal. If proper frequency and phase cycling has been employed during data acquisition, all sum and difference echoes have the same average phase. The phase estimated in block 350 is used to rotate, in phase correction block 360, the phase of all data points in the complex difference signal into the real axis. Such rotation yields the true absorption mode (real-valued) signal component. The dispersion signal component (imaginary valued) can be discarded.

Detailed Description Text (75):

Based on the parametric representations for relaxation times and diffusion characteristics of the non-wetting hydrocarbon phases which are computed, as indicated in the section "Signal Modeling and Corrections", and stored in block 365 for the oil and block 370 for the gas components. Matched filters representing the liquid and the gaseous phases are computed next in blocks 375, 380 in the echo-time domain, using the expressions:

Detailed Description Text (78):

In general, the filter functions in Eqs. (7a-7b) are not orthogonal and cannot be directly applied to the data. (See FIG. 9A) Instead, the amplitude responses to these filters are extracted from the phase-corrected difference signal $d(t)$ by solving, in block 390, the overdetermined equation system,

Detailed Description Text (79):

in a least-squares sense. The solution is found by solving the following 2.times.2 equation system for the amplitude vector x:

Detailed Description Text (80):

If the difference signal d(t) was properly scaled in p.u., the first element of the solution vector x is oil-filled porosity .PHI..sub.o, obtained in block 392, and the second is gas-filled porosity .PHI..sub.g (block 394). Calculating backwards from these numbers, the properly scaled oil and gas signatures can be reconstructed in block 395, and subtracted from the complex sum signal in block 342. The remainder is the signal originating from brine, which, as wetting phase, is sensitive to the surface-to-volume ratios in the remaining pore space available to water.

Detailed Description Text (81):

In block 400, a T.sub.2 inversion mapping is constructed, as discussed, for example in the Prammer et al. paper above. The results are used, in block 410, to estimate the T.sub.2 spectrum of the signal and in block 420 to estimate the water-bound porosity.

Detailed Description Text (82):

These ratios are indicative of the non-productible water volume held in place by capillary forces (BVI), which is computed in block 440. On the other hand, the total area under the T.sub.2 curve is interpreted as water-filled porosity .PHI..sub.w which is computed in block 420. The total NMR porosity can be computed in block 430 using the expression:

Detailed Description Text (83):

The free-fluid index as seen from the water phase is augmented by oil and gas porosity:

Detailed Description Text (84):

From .PHI..sub.NMR, BVI and FFI, a permeability estimate can be calculated in block 450, which depends only on NMR-derived quantities.

Detailed Description Text (85):

Processing of Diffusion-weighted Data

Detailed Description Text (86):

Turning back to block 330 in FIG. 7, for a diffusion-weighted measurement a complication arises from the different sampling grids employed in acquiring the data sets which make up a data pair. In this case, data from the shorter echo spacing is mapped onto the wider sampling grid by linear interpolation between complex echoes. Diffusion-weighting is taken into account to give the following matched-filters expressions:

Detailed Description Text (87):

The diffusion-weighted data is next processed following the flow graph in FIG. 7. The combined T.sub.1-weighted and diffusion-weighted measurement is advantageously used in cases where the gas filled porosity and HI are relatively low, and correspondingly the SNR of the measurement is relatively low.

Detailed Description Text (88):

Error estimates for T.sub.1-weighted and diffusion-weighted data acquisitions in accordance with a preferred embodiment of the present invention can be obtained using the following considerations. The input data consists of two data sets, weighed by different recovery times and possibly sampled with different echo spacings. Each set is individually calibrated for HI=1.0. To compute the uncertainty of the parameter estimates, it is assumed that the noise in each data set is random and has Gaussian distribution with standard deviation .sigma.=2. As indicated in blocks 350 and 360 above, a depth-averaged signal phase is computed from the complex second echo in the sum. The estimated phase is used to rotate all complex differences into the real axis. Allowing for a small error in phase estimation, the noise component in the real-valued difference signal (dt) is approximately 1.5 p.u. Gas and oil porosities are given as least-squares solutions in block 390 in FIG. 7. Formally, the least-squares solution can be written as:

Detailed Description Text (89):

The sensitivity of the solution to random errors in the input is given by the condition number of the square, positive-definite matrix A.sup.T A. The orthogonalized oil-sensitive filter function f(t)', is the first row of the

expression $(A \cdot \sup T A) \cdot \sup -1 A \cdot \sup T$. The second row of this expression contains the orthogonal filter $f(t) \cdot \sub g$, which is sensitive to the gas component. The orthogonal filter responses are shown in FIG. 10. Filter response functions are computed as follows: ##EQU3##

Detailed Description Text (90):

The average output uncertainty was determined by Monte Carlo simulation. Using 100,000 samples, and assuming parameters, $HI \cdot \sub g = 0.5$, $T \cdot \sub 1, g = 5$ s, the standard output deviation in the answer for gas filled porosity is ≈ 2.5 p.u. The uncertainty in oil-filled porosity is substantially reduced and is approximately equal to 1 p.u., dependent on $T \cdot \sub 1, o$.

Detailed Description Text (91):

As noted, in another aspect the invention uses low field gradient tools resulting in reduced static field gradients on the order of 0.3-3 gauss/cm. The modified processing sequence illustrated in FIGS. 12A-C is used in such case in a preferred embodiment.

Detailed Description Text (93):

Nomenclature A=design matrix for least-squares problem $A \cdot \sup T$ =transpose matrix of A BVI=bulk volume irreducible water, p.u. D=restricted diffusivity, $\text{cm} \cdot \sup 2 / \text{S}$ $D \cdot \sub o$ =unrestricted diffusivity, $\text{cm} \cdot \sup 2 / \text{S}$ $d(t)$ =difference function $f(t)$ =filter function FFI=free fluid index, p.u. G=magnetic field gradient, G/cm HI=hydrogen index, relative to water MPHI=apparent NMR porosity, p.u. T=absolute temperature, degree. K. $T \cdot \sub 1$ =longitudinal relaxation time, s $T \cdot \sub 1, \sup \cdot \dagger$ =pseudo transverse relaxation time, s $T \cdot \sub 2$ =transverse relaxation time, s $T \cdot \sub 2, \sup \cdot \dagger$ =apparent transverse relaxation time, s TE =CPMG echo-to-echo delay ($TE=2 \cdot \tau$), s TR =recovery time, s x =solution vector to least-squares problem $\cdot \text{PHI}$ =porosity, p.u. $\cdot \text{PHI} \cdot \sub \text{NMR}$ =corrected NMR porosity, p.u. $\cdot \text{PHI} \cdot \sub n$ =CPMG phase, $n=1$ or 2 γ =gyromagnetic ratio, $\text{rad} \cdot \sup -1$ $G \cdot \sup -1$ {character pullout}=density, $\text{g} / \text{cm} \cdot \sup 3$ σ =standard deviation τ =CPMG pulse-to-echo delay ($\tau = TE/2$), s $\tau \cdot \sub \text{eff}$ =diffusion-effective CPMG delay, s

Detailed Description Text (94):

Subscripts g=gas o=oil

Detailed Description Text (97):

FIG. 9A shows the response of the gas (block 375) and the oil (block 380) matched filters in accordance with the present invention; FIG. 9B illustrates the magnitude of the Fourier transform of the matched filters responses shown in FIG. 9A.

Detailed Description Text (98):

FIG. 10 shows the orthogonalized filter functions of the gas and the oil matched filters in accordance with the present invention.

Detailed Description Text (100):

Logging tests were performed in single-frequency and dual frequency operating modes to assess the amount of vertical and lateral motion, which could affect the accuracy of the $T \cdot \sub 1$ -weighted measurements conducted in accordance with the present invention. A similar operating procedure was already in place to set the optimum delay time between measurements in the pay zone. Data acquired under a variety of hole conditions and $T \cdot \sub 1$ values were examined; logging speeds in this particular mode were typically 300 ft/hr. In all cases, increasing the recovery time interval resulted either in a monotonic increase in NMR amplitude or in no increase. Sudden increases in amplitude at short recovery intervals, indicative of uncontrolled tool motion, were not observed.

Detailed Description Text (101):

The effect of invasion was studied by comparing results from wells drilled with water-base muds (WBM) and oil-muds (OBM). The WBM-drilled formations generally suffer high invasion and residual oil and gas saturations are low. Nevertheless, in many cases gas quantities above the detectability threshold are present, possibly due to backsaturation of gas into the invaded zone. As indicated above, another factor aiding the MRIL-RTM is the 4" blind zone into the formation. OBM filtrate generally invades less and is therefore better suited for near-borehole saturation measurements. Oil filtrate mixes with the connate oil and replaces it to a certain extent. Because the filtrate has low viscosity, OBM aids the described hydrocarbon detection method by supplying a slowly relaxing component with known $T \cdot \sub 1$. We recommend performing $T \cdot \sub 1$ and $T \cdot \sub 2$ measurements of filtrates in the laboratory

at 1 MHz to assess the effect of OBM invasion.

Detailed Description Text (103):

Log results are shown in FIG. 11. For the example illustrated in FIG. 11 NMR data for recovery times of $TR_{sub.1} = 3$ s and $TR_{sub.2} = 8$ s were acquired in separate passes with a pulse-echo spacing $\tau = 0.6$ ms. Both apparent NMR porosities are too low in the gas zone (shown in track 4). Complex echo sums and differences from these echo sets were computed. The sum had a constant phase of -2.1 rad, which was used to convert the difference signal to real-type values. Matched filters for the oil component:

Detailed Description Text (105):

were computed and applied to the data in a least-squares sense as described above. The oil-filter response was essentially zero (not shown), the gas-filter response is plotted in track 1.

Detailed Description Text (106):

Gas-corrected NMR porosity indicates that mud filtrate did not invade the sampling diameter (15" at a probe temperature of 100.degree.C.), or that gas did backsaturate into the invaded zone. In either case, the results clearly indicate the value of hydrocarbon saturation measurements near the borehole wall.

Detailed Description Text (107):

Simulation Results for Embodiments Using Low Field Gradient

Detailed Description Text (108):

The NMR response can be computed by brute force from the Bloch Equations, or, more efficiently, by a Riemannian spherical affine projection onto the complex plane. The latter procedure ignores the effects of relaxation, which is appropriate here. Some results are shown in FIG. 13 and FIG. 14.

Detailed Description Text (109):

FIG. 13 treats the case of little or no diffusion. Switching TD to a value larger than TE results in loss of signal in echo 2 and onward. This effect can be understood by considering that echoes 2, 3, etc. contain both direct spin echoes, as well as indirect ("stimulated") echoes (See, for example, Goelman and Prammer: "The CPMG Pulse Sequence in Strong Magnetic Field Gradients With Applications to Oil-Well Logging," J. Magn. Reson. A 113 (March 1995), p. 11.) The significance of this observation is that in general calibrations must be performed separately for the case when $TD=TE$ and $TD>TE$. Also, in order to recover signal-to-noise, preferably twice as many experiments per $TD>TE$ value should be performed compared with the case when $TD=TE$.

Detailed Description Text (110):

The simulation results illustrated in the figure show computed echo amplitudes for the case of no diffusion. Only the first 50 echoes are shown, more typically 100-1000 echoes would be used in accordance with a preferred embodiment. The left diagram in FIG. 13 illustrates echo amplitudes for the case $TD=TE=1$ ms. The right diagram illustrates the case when $TD=32$ ms, $TE=1$ ms. Note that the first echo has the same amplitude as in the left figure, but all other echoes are attenuated. This is a result of the loss of stimulated echoes that are not carried over to the second echo and does not reflect attenuation due to diffusion. The amount of attenuation due to stimulated echo effects is predictable and can be calibrated in a preferred embodiment on a test sample.

Detailed Description Text (111):

FIG. 14 shows the strong attenuation effect if fast diffusion is present. A (weak) gradient of 1 gauss/cm and a diffusion coefficient of 10×10^{-3} cm²/sec were assumed for these simulations. The simulation results show computed echo amplitudes for the case of rapid diffusion ($D=10 \times 10^{-3}$ cm²/s), typical of vapor phase under reservoir conditions). The left diagram illustrates echo amplitudes for the case $TD=TE=1$ ms. The right diagram illustrates the case when $TD=32$ ms, $TE=1$ ms. After accounting for the loss of stimulated echoes, the gas signal has been attenuated to 14% of its original value. The gas signal can be recovered in accordance with a preferred embodiment by individually fitting each echo train and comparing total amplitudes, or by subtracting the amplitudes of corresponding echoes. Thus, by subtracting echo-by-echo the right diagram from the left diagram (ignoring all echoes occurring at times less than TD), the gas phase signal can be isolated.

Detailed Description Text (112):

Appendix A provides listings of several NMR Simulation Programs in the Matlab programming language, which can be used in accordance with the present invention to perform the above-referred computations.

Detailed Description Text (114):

Job Planning. In accordance with the present invention job planning consists of estimating diffusivity values for gas, oil and free water and selecting appropriate TD and TE values based on forward-modeling of signal components to achieve maximum contrast between fluid phases. The simple calculation shown above is an example. Following is a brief description of a model-based linear inversion algorithm that can be used in accordance with a preferred embodiment for the forward modeling of signal components.

Detailed Description Text (116):

Let a, b, c, \dots denote the indices for the free fluid components, e.g., gas, water and oil. Let also $S_{sub.i}$ ($i=a, b, c, \dots$) denote a signal component and let $V_{sub.i}$ ($i=a, b, c, \dots$) be the volume occupied by a fluid component. S and V are related as follows:

Detailed Description Text (117):

where K is a calibration constant containing the system gain, the gyromagnetic ratio, the operating frequency, etc.; T is the absolute temperature; $HI_{sub.i}$ is the hydrogen index (i.e., hydrogen density relative to water) of the i -th signal component; $P_{sub.i}$ is a component-specific polarization term, typically of the form $(1 - \exp(-T_w/T1_{sub.i}))$, where T_w is the pre-measurement wait time (polarization time) and $T1_{sub.i}$ is the $T1$ time constant of the i -th component.

Detailed Description Text (118):

Measurements are made with at least three different values for TD. In a specific example: $TD=1, 32$ and 70 ms.

Detailed Description Text (119):

The echo spacing ΔTE is held constant (example: $TE=1$ ms). All echoes occurring before 70 ms are ignored to eliminate the influence of fast-decaying components from water or oil phases. A relatively short acquisition window is selected (example: 10 - 100 ms). Within this time window, the inherent $T2$ decay is small for all free-fluid components and all echoes within the time window can be summed and averaged. This step improves the SNR by a factor of 3 - 10 . The net result are three numbers, representing the averaged observed signal amplitude after 70 ms under the conditions of $TD=1, 32$ and 70 ms. Let $A_{sub.j}$, ($j=1, 2, 3, \dots$) be these numbers. The signals $S_{sub.i}$ and the measured amplitudes $A_{sub.j}$ are related to each other as follows:

Detailed Description Text (121):

The matrix elements $M_{sub.ji}$ encode the response of each fluid component to a specific value of TD. There are given by

Detailed Description Text (125):

And, finally, the fluid volumes themselves:

Detailed Description Text (127):

Postprocessing. In accordance with a preferred embodiment, in postprocessing, calibrations are applied to eliminate stimulated echo effects that distort echo amplitudes. Next, the echo trains for various TD values are processed either simultaneously or in pairs. If processed in pairs, only the common time windows (from the longest TD interval onward) are considered. The subtraction of corresponding echoes enhances a particular fluid phase: the gas phase between the two shortest TD values; the water phase between the next TD pair, and the oil phase from the longest TD value only without subtraction. Lastly, correction values are applied that account for (a) incomplete polarization, (b) incomplete suppression by diffusion, and (c) hydrogen density.

Detailed Description Text (128):

The low-field gradient processing method in accordance with the present invention can be further combined with the frequency hopping method using variable wait times. FIG. 15 is an illustration of a multi-frequency TD/TE pulse sequence. Each box in FIG. 15 represents a TD/TE sequence. In a preferred embodiment, the TD parameter is systematically cycled through all of its values. The wait time T_w is kept constant

and is typically in the range of 8 to 12 seconds, although other values may be used in specific embodiments. FIG. 15 A shows an implementation of the method of the present invention using a modified TD/TE pulse sequence for two frequencies (i.e., two sensitive volumes). FIG. 15B illustrates the use of the modified pulse sequence in the case of four operating frequencies (sensitive volumes). Signal components with long $T_{sub.1}$ relaxation values can be selectively attenuated by choosing wait times between CPMG and modified CPMG trains that are short compared to $T_{sub.1}$.

Detailed Description Paragraph Equation (22):

$M_{sub.ji} = \exp(-1/12(\gamma_{sup.2} G_{sup.2} TD_{sub.j} D_{sub.i}))$. γ is the gyromagnetic ratio (2 π .4258 sec.⁻¹ /gauss), G is the field gradient, and $D_{sub.i}$ is the diffusivity of the i -th component. Continuing with the example: $G=1$ gauss/cm, and $D_{sub.1}=10^{-3}$ cm.² /s for the vapor (gas) phase, $D_{sub.2}=10^{-4}$ cm.² /s for the free-water phase, and $D_{sub.3}=10^{-5}$ cm.² /s for the oil phase.

Detailed Description Paragraph Table (2):

TABLE 2 Spin Lattice Relaxation Self Diffusion coeff. Fluid (sec) (cm.² /sec) parameters/units Methane $T_{sub.1,g} = 25.10$ $\rho_{sub.1,17} D_{sub.0g} = 8.5.10$ $\tau_{sub.0.9} / \rho$. Gas density ρ . in gramm/cc; T-abs temp in Kelvin Oil $T_{sub.1,o} = 1.2(T/298)/\eta$. $D_{sub.0,o} = 1.3(T/298)/\eta$. η is oil viscosity in cp; T-abs temp in Kelvin Water $T_{sub.1,w} = 3(T/298)/\eta$. $D_{sub.0,w} = 1.2(T/298)/\eta$. Same as above

Detailed Description Paragraph Table (3):

$D = 10^{-3}$ cm.² /s for the vapor (gas) phase, $D = 10^{-4}$ cm.² /s for the free-water phase, and $D = 10^{-5}$ cm.² /s for the oil phase. $TE = 0.001$ sec, $G = 1$ gauss/cm, $g = 2\pi 4258$ sec.⁻¹ /gauss (proton gyromagnetic ratio).

Detailed Description Paragraph Table (4):

TD value results in signals from... 1 ms (=TE) all fluid phases, weighted only hydrogen density and incomplete polarization (in case of short wait times), 32 ms free water, oil and some bound water (attenuated by intrinsic $T_{sub.2}$), 70 ms oil only (attenuated by intrinsic $T_{sub.2}$).

Detailed Description Paragraph Table (5):

TABLE 3 parameters for example data. gas temperature: 100.degree. C. gas pressure: 9000 psi gas type: CH.₄ CH.₄ density: $\rho = 0.26$ g/cm.³ CH.₄ hydrogen index: $HI_{sub.g} = 0.6$ longitudinal relaxation $T_{sub.1} = 6$ s time: unrestricted diffusivity: $D_{sub.0} = 0.7$ times. 10^{-3} cm.² /s diffusion restriction (est.): $D/D_{sub.0} = 0.8$ magnetic field gradient $G = 18$ G/cm effective pulse-echo $\tau_{sub.0.65}$ ms spacing: apparent transverse $T_{sub.2}$ $\tau_{sub.2}$ = 60 ms relaxation: $T_{sub.1} / T_{sub.2}$ contrast: about.100

Detailed Description Paragraph Table (6):

APPENDIX A % CPMG.M - - - CPMG sequence % % NMR Simulation Program. % % .COPYRGT. Copyright, M. G. Prammer, NUMAR Corp., 1991, 1992, 1993. % Modification History: % Oct. 1991, MGP, Written. % Jul. 1992, MGP, modified pulsing. %
 %%% experimental parameters %%% echo on; $T_2 = 1e6$; % T_2 sec Assumed true T_2 $TE = 1e-3$; % TE sec Echo time $NE = 50$; % NE Number of echoes $t_{90} = 100e-6$; % t_{90} sec 90-degree pulse width $t_{180} = 160e-6$; % t_{180} sec 180-degree pulse width $AT = TE - t_{180}$; % AT sec Acquisition time $dt = 20e-6$; % dt sec Dwell time $A = 1/(2*t_{180})$; % A Hz Pulse amplitude $fmin = -5000$; % $fmin$ Hz Leftmost freq sample $fmax = 5000$; % $fmax$ Hz Rightmost freq sample $df = 40$; % df Hz Frequency resolution $fjitter = 10$; % $fjitter$ Hz Random frequency jitter figure(1); echo off; %%% %%%
 %%% $t=0:dt:AT$; % create acquisition time axis $f=fmin:df:fmax$; % create frequency axis $[dum,NF]=size(f)$; % NF . . . no of frequency points $sx=[]$; % real channel signal $sy=[]$; % imaginary channel signal % establish equilibrium $mx=zeros(size(f))$; $my=zeros(size(f))$; $mz=ones(size(f))$; % 90 pulse; $phase = 90$ $[mx,my,mz]=pulsim(j*A,t_{90},f,mx,my,mz)$; $[mx,my,mz]=evolve(T_2,t_{90}+(TE-t_{90}-t_{180})/2,f,mx,my,mz)$; %!!! for $nr=1:NE$, %fprintf('Echo %.0f.backslash.n',nr*1.0); % 180 pulse; $phase = 0$ $[mx,my,mz]=pulsim(A,t_{180},f,mx,my,mz)$; $[tmpx,tmpy]=observe(dt,AT,f,mx,my,mz)$; % compute response $[mx,my,mz]=evolve(T_2,TE-t_{180},f,mx,my,mz)$; % evolve $[mx1,my1,mz1]=evolve(T_2,(TE-t_{180})/2,f,mx,my,mz)$; % echo profile $sx=[sx ; tmpx]$; $sy=[sy ; tmpy]$; $s=sqrt(sx.^2+sy.^2)$; $plot(t,sx)$; $grid$; $xlabel('Time in sec after pi pulse')$; $drawnow$; % introduce frequency jitter to mask numerical discretization $f = f+fjitter*randn(size(f))$; end % create entire timeline $tall=[]$; for $nr=1:NE$,

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Hou et al., "Nuclear Magnetic Resonance Logging Methods for Fluid Typing," Society of Petroleum Engineers, Inc., SPE 48896, 1998.

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CLAIMS:

1. A method for making nuclear magnetic resonance (NMR) measurements of a geologic formation using a NMR logging tool, comprising the steps of: (a) providing a static magnetic field in a volume of said formation; (b) applying a modified CPMG pulse sequence according to the expression:

$$W_{sub.i} - \pi/2 - TD_{sub.j} / 2 - \pi - TD_{sub.j} / 2 - echo - [TE/2 - \pi - TE/2 - echo]_{sub.k}$$
 where $W_{sub.i}$ is a variable delay with $i \geq 0$; $TD_{sub.j}$ is variable echo spacing, $j \geq 1$; $TE/2$ is the Carr-Purcell echo spacing, $TD_{sub.j} > TE$; $k = 1, \dots, N$; and (c) measuring the induced NMR echo signals.

2. The method of claim 1 further comprising the step of processing the induced NMR echo signals to derive petrophysical properties of the formation.

3. The method of claim 1 further comprising the step of selecting the variable echo spacing $TD_{sub.j}$ such that the application of the modified CPMG pulse sequence causes the loss of pre-determined fast diffusion components of the measured NMR echo signals.

5. The method of claim 3, wherein $TD_{sub.j}$ is selected to cause the loss of signals associated with the gas phase and the water phase.

10. The method of claim 1 further comprising the step of pairwise subtracting NMR echo signals associated with different $TD_{sub.j}$'s.

11. The method of claim 7 further comprising the step of separating the gas, oil and water signal components.

12. A method for making nuclear magnetic resonance (NMR) measurements of a geologic formation, comprising the steps of: (a) providing a static magnetic field in a volume of said formation; (b) applying oscillating magnetic fields according to at least one modified CPMG pulse sequence characterized by having at least one first echo spacing TD and a second echo spacing TE; wherein the at least one first echo spacing TD is selected to correspond to diffusion characteristics of fluids in the formation and cause corresponding amplitude loss in induced NMR signals, and TE is relatively short, such that diffusion in the corresponding induced NMR echo signals is substantially negligible; (c) measuring the induced NMR echo signals; (d) determining the amount of amplitude loss resulting from at least one TD interval; (e) computing diffusion properties of fluids in the formation based on the determined amplitude loss.

14. The method of claim 12 further comprising the step of processing the induced NMR echo signals to derive petrophysical properties of the formation.

16. The method of claim 12, wherein TD is selected to cause the loss of signals associated with the gas phase and the water phase.

20. The method of claim 12 further comprising the step of pairwise subtracting NMR echo signals associated with different TD's to separate different fluid phases present in the formation.

21. The method of claim 20 further comprising the step of separating gas, oil and water signal components present in the formation.

22. The method of claim 12 further comprising the step of estimating diffusivity values for gas, water and oil phases in the formation, and selecting values for the TD and TE echo spacings based on the estimated diffusivity values.

23. The method of claim 22, wherein the selection of values for the TD and TE echo spacings is based on forward-modeling of signal components to achieve maximum contrast between fluid phases.

24. The method of claim 12 further comprising the step of applying calibrations to eliminate stimulated echo effects that distort echo amplitudes.

25. The method of claim 12, wherein in step (e) echo trains for different TD values are processed either simultaneously or in pairs.

26. The method of claim 25, wherein echo trains for different TD values are processed in pairs, and only common time windows from the longest TD interval onward are considered in the step of processing.

27. The method of claim 26 further comprising the step of subtracting of corresponding echoes to enhance a particular fluid phase.

28. The method of claim 27, wherein the gas phase is enhanced by subtracting the two shortest TD values; the water phase between the next TD pair, and the oil phase from the longest TD value only without subtraction.

29. The method of claim 12, further comprising applying correction values that account for (a) incomplete polarization, (b) incomplete suppression by diffusion, and (c) hydrogen density.

30. A system for making nuclear magnetic resonance (NMR) measurements of a geologic formation, comprising: (a) means for providing a static magnetic field in a volume of said formation; (b) means for applying oscillating magnetic fields according to at least one modified CPMG pulse sequence characterized by having at least one first echo spacing TD and a second echo spacing TE; wherein the at least one first echo spacing TD is selected to correspond to diffusion characteristics of fluids in the formation and cause corresponding amplitude loss in induced NMR signals, and TE is relatively short, such that diffusion in the corresponding induced NMR echo signals is substantially negligible; (c) means for measuring the induced NMR echo signals; (d) means for determining the amount of amplitude loss resulting from at least one TD interval; and (e) means for computing diffusion properties of fluids in the

formation based on the determined amplitude loss.



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DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatusAbstract Text (1):

Technique and apparatus are disclosed for identifying characteristics of hydrocarbons, such as distinguishing light and heavy formation oil, in formations surrounding an earth borehole. The technique and apparatus can also be used for determining residual oil saturation, permeability, and bound water volume. An embodiment of the method of the invention includes the following steps: providing a nuclear magnetic resonance logging device that is moveable through the borehole; providing, from the logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations; processing the received spin echoes to produce a $T_{sub 2}$ distribution; computing a magnetic resonance porosity from the $T_{sub 2}$ distribution; deriving a measure of total porosity of the formations; and comparing the magnetic resonance porosity with the total porosity.

Brief Summary Text (2):

This invention relates to apparatus and techniques for determining characteristics of earth formations surrounding a borehole and, more particularly, to a method and apparatus for nuclear magnetic resonance borehole logging to determine characteristics including one or more of the following: the nature of formation hydrocarbons, residual oil saturation, permeability, and bound water volume. The invention also relates to MR logging with improved logging speed.

Brief Summary Text (4):

General background of nuclear magnetic resonance well logging [also called magnetic resonance (MR) logging] is set forth in copending U.S. patent application Ser. No. 08/873,582, assigned to the assignee hereof, and in U.S. Pat. No. 5,023,551. Briefly, in nuclear magnetic resonance operation, the spins of nuclei align themselves along an externally applied static magnetic field. This equilibrium situation can be disturbed by a pulse of an oscillating magnetic field (e.g. an RF pulse), which tips the spins away from the static field direction. After tipping, two things occur simultaneously. First, the spins precess around the static field at the Larmor frequency, given by $\omega_{sub 0} = \gamma B_{sub 0}$, where $B_{sub 0}$ is the strength of the static field and γ is the gyromagnetic ratio. Second, the spins return to the equilibrium direction according to a decay time T_1 , the spin lattice relaxation time. For hydrogen nuclei, $\gamma/2\pi = 4258$ Hz/Gauss, so, for example, for a static field of 235 Gauss, the frequency of precession would be 1 MHz. Also associated with the spin of molecular nuclei is a second relaxation, T_2 , called the spin-spin relaxation time. At the end of a ninety degree tipping pulse, all the spins are pointed in a common direction perpendicular to the static field, and they all precess near the Larmor frequency. However, because of molecular interactions, each nuclear spin precesses at a slightly different rate. T_2 is a time constant of this "dephasing".

Brief Summary Text (5):

A widely used technique for acquiring NMR data both in the laboratory and in well logging, uses an RF pulse sequence known as the CPMG (Carr-Purcell-Meiboom-Gill) sequence. [See Meiboom, S., Gill, D., 1958, "Modified Spin Echo Method for Measuring Nuclear Relaxation Times", Review of Scientific Instruments, 29, 688-691]. As is well known, after a wait time that precedes each pulse sequence, a ninety degree pulse causes the spins to start precessing. Then a one hundred eighty degree pulse is applied to keep the spins in the measurement plane, but to cause the spins which are dephasing in the transverse plane to refocus. By repeatedly reversing the spins

using one hundred eighty degree pulses, a series of "spin echoes" appear, and the train of echoes is measured and processed, for example to obtain a T_{sub 2} distribution of fluid components of the formations.

Brief Summary Text (6):

Magnetic resonance logging has added a new dimension to formation evaluation. The MR measurement is sensitive to total fluid content, to the intrinsic properties of the fluids, and to the environments in which the fluids reside in the pore space of porous rock. There are many applications of magnetic resonance tools, and among the most common and important are the determination of capillary and clay bound water volumes and the estimation of permeability. Bound water analysis is of central interest to the log interpreter because it helps predict the potential water cut of a formation volume, and is a major factor in the perforation decision. A continuous permeability log can provide an estimation of potential production rate and also indicates flow barriers and thief zones. These log outputs are difficult to obtain reliably with other logging tools, and hence may be termed "MR-unique".

Brief Summary Text (7):

One limitation of MR tools is their slow logging speed. Magnetic resonance logging uses a cyclic measurement consisting of a wait time followed by an echo acquisition period. Conventional MR data are presently acquired with

Brief Summary Text (8):

wait times sufficiently long to substantially polarize all fluid protons in the formation. Protons in gas, light oil, oil base mud filtrates, and vug water polarize very slowly. Therefore, very long wait times have been used when logging formations in which those fluids are present. The long wait times necessarily contribute to slow logging speeds. Thus, while MR tools provide important additional information, it can be at the cost of wellsite efficiency.

Brief Summary Text (10):

Heretofore it has been considered difficult or impossible to estimate residual oil saturation in wells drilled with oil base mud. This is particularly true when the native oil has a low downhole viscosity, which renders it difficult or impossible to distinguish native fluids from invaded fluids on the basis of existing magnetic resonance T_{sub 2} measurements.

Brief Summary Text (11):

It is among the objects of the present invention to overcome limitations of prior art MR techniques by determining residual oil saturation and other formation characteristics in wells drilled with oil base mud. It is also among the objects of the invention to improve logging speed (e.g. for a given precision and/or vertical resolution) of MR logging. It is also among the objects of the invention to provide a technique for determining when formation permeability may be overestimated in certain types of formations.

Brief Summary Text (14):

Magnetic resonance tools are extreme examples of cyclic tools: the measurement cycle is longer and more complicated than for any other logging tool. In a typical MR measurement cycle, and as referenced in the background portion hereof, permanent magnets within the tool polarize the hydrogen nuclei of formation fluids during a "wait time". Then, an antenna broadcasts a series of pulses of high frequency magnetic field. Return spin echoes from the formation are detected after the second and each subsequent pulse in a CPMG pulse sequence.

Brief Summary Text (15):

In a known type of MR logging device to be referenced hereinbelow, the wait-acquisition cycles are collected in phase alternated pairs (PAPs). A phase shift of the RF carrier of one pulse in the sequence reverses the sense of the CPMG acquisition [See Sezginer, A., Kleinberg, R. L., Fukuhara, M., Latour, L. L., 1991, "Very Rapid Simultaneous Measurement of Nuclear Magnetic Resonance Spin-Lattice Relaxation Time and Spin-Spin Relaxation Time", Journal of Magnetic Resonance 92, 504-527; U.S. Pat. No. 5,023,551.] Taking the difference between the positive and negative CPMG's echo-by-echo doubles the size of the signal and eliminates baseline and several spin-dynamics errors.

Brief Summary Text (19):

The sandstone logging mode is generally satisfactory when the formation hydrogen can be polarized during the 1.3 second wait time. Then the logging tool can provide a

complete suite of MR measurements, including porosity, pore size distribution, and other useful log outputs. However, in some circumstances, the 1.3 second wait time is inadequate to fully polarize the formation. This is the case when formations have long longitudinal relaxation times, $T_{sub.1}$. As noted in the background hereof, examples are reservoirs with light oil or gas, those drilled with oil base muds, or those with vugs. In such cases, $T_{sub.1}$ is usually equal to its bulk fluid value, which can be several seconds. [See Kleinberg, R. L. Vinegar, H. J., 1996, "NMR Properties of Reservoir Fluids", Log Analyst November-December 1996. pg. 20-32.] The wait time must be several times longer than the longest formation $T_{sub.1}$ to obtain complete information. This increases the cycle time, T . To maintain precision and vertical resolution, the logging speed must be reduced. See, for example, Morriss, C. E., Deutch, P., Freedman, R., McKeon, D., Kleinberg, R. L., 1996, "Operating Guide for the Combinable Magnetic Resonance Tool", Log Analyst, November-December 1996, pg. 53-60, which describes an MR tool operating in an oil base mud mode with a logging speed of 200 ft/hr.

Brief Summary Text (20):

Magnetic resonance logging tools are characterized by considerable flexibility in measurement modes. Measurement can be tailored to the objectives of the logging program. In an illustrated embodiment and examples hereof, wells drilled with oil base mud are considered. Neutron, density, resistivity and gamma ray tools can efficiently provide porosity, lithology, and deep saturation information. Permeability and precise values of bound water volume used for the determinations hereof are obtained by magnetic resonance logging. Rig time expense dictates the most rapid acquisition possible consistent with requirements of enhanced precision and good vertical resolution, and rapid acquisition is an advantageous feature of the invention.

Brief Summary Text (21):

As is well known, the volume of bound water at a given air-brine capillary pressure is associated with nuclear magnetic resonance signals that decay with a $T_{sub.2}$ less than a formation-dependent $T_{sub.2}$ cutoff. In sandstones, for an air-brine capillary pressure of 100 psi (700 kPa), the $T_{sub.2}$ cutoff is often about 33 msec, but can be higher or lower [see Straley, C., Rossini, D., Vinegar, H., Tutunjian, P., Morriss, C., 1997, "Core Analysis by Low Field NMR", Log Analyst, March-April 1997, pg. 84-94]. The $T_{sub.1}$ associated with this part of the porosity is often about 1.5 times longer than $T_{sub.2}$ [see Kleinberg, R. L., Straley, C., Kenyon, W. E., Akkurt, R., Farooqui, S. A., 1993, "Nuclear Magnetic Resonance of Rocks: $T_{sub.1}$ vs. $T_{sub.2}$ ", Society of Petroleum Engineers Papers 26470; Straley, C., Morriss, C. E., Kenyon, W. E., Howard, J. J., 1995, "NMR in Partially Saturated Rocks", Log Analyst, January-February 1995, pg. 40-56]. A reduced wait time, of duration a few times longer than longest $T_{sub.1}$ of the bound fluid, will completely polarize the bound water in the formation. Note also that fewer echoes are needed to characterize relaxation time components shorter than $T_{sub.2}$ cutoff than are required to characterize the entire $T_{sub.2}$ distribution.

Brief Summary Text (22):

When the wait time is short, those formation fluids having long $T_{sub.1}$'s are not completely polarized, i.e. they are not fully represented in the subsequent CPMG echo train. As is known in the art, for a fluid component characterized by $T_{sub.1i}$, the apparent signal amplitude is given by $W \cdot A_{sub.i}$ where W is the wait time, $A_{sub.i}$ is the signal strength (in porosity units) associated with a formation fluid i having polarization time $T_{sub.1i}$, and $A_{sub.0i}$ is the signal strength for that fluid in the limit $W \rightarrow \infty$. If W is not several times longer than $T_{sub.1i}$, the signal strength $A_{sub.i}$ is not representative of the volume of that fluid.

Brief Summary Text (23):

Laboratory measurements on water saturated rocks have shown that $T_{sub.1}$ can be estimated by $T_{sub.1} = \xi \cdot T_{sub.2}$, where $1 < \xi < 3$. Then, equation (3) can be written as $W \cdot A_{sub.i}$. Conventional processing with the type of MR tool described herein automatically accounts for this factor. The result is functionally equivalent to correcting the $T_{sub.2}$ distribution; that is $P(T_{sub.2i}) \cdot \xi$ where $P(T_{sub.2i})$ is the uncorrected $T_{sub.2}$ distribution and $P(T_{sub.2i})$ is the displayed distribution. The default value, $\xi = 1.5$, is appropriate for many water saturated rocks.

Brief Summary Text (24):

In the presence of light oil or oil base mud, when the $T_{sub.2}$ distribution is distorted by the effects of reduced cycle time, the standard polarization correction

is inappropriate. It is preferable to use equation (3) to recover the true amplitude of fluid components with long $T_{sub.1}$'s. The polarization correction would then be ##EQU5## Note that a fixed value of $T_{sub.1}$ --that is, the longer relaxation time of the oil phase--is used in this equation. This correction should only be applied to that part of the $T_{sub.2}$ distribution which represents the oil phase. The bound water (in water wet rock) has a very short relaxation time, and clearly the $T_{sub.1}$ of the oil phase should not be applied to it. $T_{sub.1}$ is not measured directly by MR tools, but in many cases it can be estimated from the bulk properties of the fluids at reservoir conditions [see Kleinberg, R. L. Vinegar, H. J., 1996, "NMR Properties of Reservoir Fluids", Log Analyst November-December 1996. pg. 20-32].

Brief Summary Text (25):

Cycle time can also be reduced by reducing the number of echoes acquired in each CPMG. A long acquisition time, $N \cdot TE$, is required if good definition of long $T_{sub.2}$ components is required. To obtain accurate values of bound water volume, it is only necessary to resolve components having $T_{sub.2}$ less than $T_{sub.2cutoff}$. For $TE=0.32$ msec, as few as 100 echoes are adequate to define the $T_{sub.2}$ distribution below 30 msec.

Brief Summary Text (27):

In accordance with an embodiment of the invention, there is disclosed a method for identifying characteristics of hydrocarbons (e.g. distinguishing light and heavy formation oil) in formations surrounding an earth borehole, comprising the following steps: providing a nuclear magnetic resonance logging device that is moveable through the borehole; providing, from the logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations; processing the received spin echoes to produce a $T_{sub.2}$ distribution; computing a magnetic resonance porosity from the $T_{sub.2}$ distribution; deriving a measure of total porosity of the formations; and comparing the magnetic resonance porosity with the total porosity. Residual oil saturation can also be obtained as a function of the comparison.

Brief Summary Text (28):

In a preferred embodiment of the invention, the polarization wait time, W , of said cycles of magnetic pulse sequence is short enough to incompletely polarize the protons in an investigation region of the formations. In this embodiment, the wait time, W , is in the range 0.1 second to 1 second. Also in this embodiment, the step of comparing the magnetic resonance porosity with the total porosity comprises comparing the respective porosities in a water-bearing zone of the formations and comparing the respective porosities in an oil-bearing zone of the formations. In a form of the preferred embodiment, the following steps are also performed: developing a free/bound fluid cutoff of the $T_{sub.2}$ distribution and applying a polarization correction to the free fluid components of the $T_{sub.2}$ distribution before computing the magnetic resonance porosity from the $T_{sub.2}$ distribution. In this form of the preferred embodiment, the step of comparing the magnetic resonance porosity with the total porosity comprises comparing the respective porosities in a water-bearing zone of the formations and comparing the respective porosities in an oil-bearing zone of the formations.

Drawing Description Text (3):

FIG. 2 is a cross-sectional diagram of a portion of the nuclear magnetic resonance logging device of FIG. 1.

Drawing Description Text (4):

FIG. 3 is a perspective view of the RF antenna of the FIG. 1 nuclear magnetic resonance logging device.

Drawing Description Text (7):

FIG. 6 shows $T_{sub.2}$ distributions [graph (a)] and cumulatives of $T_{sub.2}$ distributions [graph (b)] for laboratory NMR measurements on a mixture of hexane and nickel chloride for different wait times.

Drawing Description Text (8):

FIG. 7 shows NMR fluid volume (normalized by true volume) versus $T_{sub.1}$ for three values of wait time W .

Detailed Description Text (2):

Referring to FIG. 1, there is shown an apparatus for investigating subsurface formations 31 traversed by a borehole 32, which can be used in practicing

embodiments of the invention. The borehole 32 is typically filled with a drilling fluid or mud which contains finely divided solids in suspension, and mudcake 16 is shown on the walls of the borehole. The invention has particularly advantageous application when the mud is oil base mud.

Detailed Description Text (3):

A magnetic resonance investigating apparatus or logging device 30 is suspended in the borehole 32 on an armored cable 33, the length of which substantially determines the relative depth of the device 30. Also shown in FIG. 1 as part of the logging string are further logging devices represented by reference numerals 60, 70, and 80. In the present embodiment the device 60 represents a density and/or neutron logging device (although it may alternatively be a sonic device or other logging device for obtaining total porosity), the device 70 is a resistivity logging device, and the device 80 is a gamma ray logging device. It will be understood that measurements from these and/or other logging devices can, if desired, be obtained from separate logging runs with these and/or other logging devices or from other sources. The length of cable 33 is controlled by suitable means at the surface such as a drum and winch mechanism (not shown). Surface equipment, represented at 7, can be of conventional type, and can include a processor subsystem and communicates with the all the downhole equipment. It will be understood that processing can be performed downhole and/or uphole, and that some of the processing may be performed at a remote location. Also, while a wireline is illustrated, alternative forms of physical support and communicating link can be used, for example in a measurement while drilling system. As described for example in the U.S. Pat. No. 5,055,787, the magnetic resonance logging device 30 has a face 14 shaped to intimately contact the borehole wall, with minimal gaps or standoff, and a retractable arm 15 which can be activated to press the body of the tool 13 against the borehole wall during a logging run, with the face 14 pressed against the wall's surface. Although the tool 13 is shown as a single body, the tool

Detailed Description Text (5):

The magnetic resonance logging device 30 includes a magnet array 17 and an RF antenna 18 positioned between the array 17 and the wall engaging face 14. Magnet array 17 produces a static magnetic field $B_{sub.0}$ in regions surrounding the tool 13. The antenna 18 produces, at selected times, an oscillating magnetic field $B_{sub.1}$ which is focussed into formation 12, and is superposed on the static field $B_{sub.0}$ within those parts of formation opposite the face 14. The "volume of investigation" of the tool, shown in dotted lines in FIG. 3, is a vertically elongated region directly in front of tool face 14. As described in the referenced Patent, the tool 13 can make measurements by magnetically tipping the nuclear spins of particles in formation 12 with a pulse of oscillating field $B_{sub.1}$, and then detecting the precession of the tipped particles in the static field $B_{sub.0}$ within the volume of investigation over a period of time. Reference can also be made to Morriss, C. E., Deutch, P., Freedman, R., McKeon, D., Kleinberg, R. L., 1996, "Operating Guide for the Combinable Magnetic Resonance Tool", Log Analyst, November-December 1996, pg. 53-60.

Detailed Description Text (6):

FIG. 2 shows a magnet array 17 of the type disclosed in an embodiment of the referenced '787 Patent. The magnet array includes two permanent magnets 24 and 26, which are mounted generally parallel to each other within a metal alloy body 27. The body 27 should be of a material having low magnetic permeability, so as to not interfere with the static magnetic field. Magnets 24 and 26 are slabs which are elongated in the longitudinal direction of the borehole. The magnetic poles of each magnet are not on the smallest faces of the slab, commonly viewed as the ends of a bar magnet. Instead, the poles appear on the two opposing edges of the slab magnet and point to the left and right, respectively, in the Figure. Therefore, within the formation 12, the magnetic field $B_{sub.0}$ surrounding the magnets remains fairly constant along the longitudinal direction of the borehole axis. In the illustration of FIG. 2, magnets 24, 26 are symmetrically mounted in the two sides of the body 27 with the north poles facing the same direction, that is, the direction of the face 14 of the tool. One or more further permanent magnets can be used.

Detailed Description Text (8):

In the referenced '787 Patent, the antenna 18 is used both as an RF transmitter to produce an oscillating magnetic field in the formations, and as a receiving antenna to detect coherent magnetic signals emanating from precessing protons (spins) after the oscillating field is terminated. The antenna, which has a body 29 and an elongated center probe 42, across which signals are applied and detected, serves

effectively as a current loop which produces an oscillating magnetic field $B_{sub.1}$ (see FIG. 4) within the volume of investigation that is perpendicular to the static magnetic field, $B_{sub.0}$ (which is radial in the volume of investigation). The body 29 is trough-shaped and has end plates 40, 41 with the center conductor or probe 42 extending from one end plate 40 to the other end plate 41, parallel to and centered in the semi-cylindrical trough 29. The U.S. Pat. No. 5,153,514 discloses that the trough antenna, which can be filled with a ferrite, can have an inner conductive shell that is separated from a steel body by a rubber layer, which suppresses magnetoacoustic ringing. It will be understood that various other types of magnetic resonance logging equipment can be used in practicing the invention.

Detailed Description Text (10):

To illustrate the effect of cycle time reduction, roughly equal amounts of hexane ($T_{sub.1} = T_{sub.2} = 1.80$ sec) and water doped with NiCl ($T_{sub.1} = T_{sub.2} = 0.022$ sec) were placed together in a sample tube and nuclear magnetic resonance measurements performed. The results are shown in FIG. 6. Run #1 (solid line) used wait=4 sec and 1800 echoes, Run #2 (dotted line) used wait=0.25 sec and 300 echoes. Graph (a) shows $T_{sub.2}$ distributions and graph (b) shows cumulatives of the distributions. No polarization correction was applied. The $T_{sub.2}$ distribution found from the long cycle time measurement shows two distinct peaks corresponding to water and hexane. The short cycle time measurement underestimates the quantity of long-relaxation-time fluid while capturing all the information associated with short relaxation time fluid. The $T_{sub.2}$ distribution for the hexane (like an oil signal) is considerably distorted when only 300 echoes are collected, as this number of echoes is not sufficient to define the details at the long- $T_{sub.2}$ end of distribution. The standard polarization correction of Equation (5) can yield erroneous results unless artificial values of ρ are used. Instead, the fixed $T_{sub.1}$ correction of Equation (6) should be applied to the long- $T_{sub.2}$ part of the relaxation time distribution.

Detailed Description Text (11):

On a local basis, permeability sometimes correlates with porosity. In general, however, permeability depends on rock fabric, which can be independent of porosity. Magnetic resonance is an accepted method of probing rock microgeometry, and a number of permeability relations based on magnetic resonance have been found useful as follows [see Morriss, C. E., Deutch, P., Freedman, R., McKeon, D. Kleinberg, R. L., 1996, "Operating Guide for the Combinable Magnetic Resonance Tool", Log Analyst, November-December 1996, pg. 53-60]:

Detailed Description Text (12):

Permeability can also be estimated by Equation (8) from short cycle MR measurements, using $FFI = \rho \cdot BFV$, where the bound fluid volume is measured by magnetic resonance, and porosity is measured by other tool(s). ##EQU7## There is some ambiguity in exactly which porosity is to be used; this point having been discussed by Singer et al. [see Singer, J. M., Johnston, L., Kleinberg, R. L., Flaum, C., 1997, "Fast NMR Logging for Bound Fluid and Permeability", SPWLA 38th Annual Logging Symposium, Paper YY]. In the present embodiment, the porosity used is density porosity $\rho_{sub.D}$, or, in the presence of gas, the neutron-density crossplot porosity $\rho_{sub.T}$.

Detailed Description Text (13):

Recent advances in MR tools, measurement techniques, and signal processing [see e.g. Prammer, M. G., Drack, E. D., Bouton, J. C., Gardner, J. S., 1996, "Measurements of Clay Bound Water and Total Porosity by Magnetic Resonance Logging", Log Analyst, November-December 1996, pg. 61-69; Freedman, R., Boyd, A., Gubelin, G., McKeon, D., Morriss, C. E., Flaum C., 1997, "Measurement of Total NMR Porosity Adds New Value to NMR Logging", SPWLA 38th Annual Logging Symposium, Paper 00] have dramatically improved the measurement of bound fluid volumes. Now, fluids having $T_{sub.2}$ relaxation times of 0.5 msec or lower are included in the bound fluid volume (BFV). With these improvements, MR porosity agrees with density porosity in most shale intervals. Since all shale porosity is bound fluid, it is usually found that $\rho_{sub.D} = BFV$ in shales. Thus, Equation (9) estimates zero permeability in typical shales.

Detailed Description Text (14):

Despite recent improvements in measuring porosity components with very short $T_{sub.2}$, magnetic resonance measurements can still underestimate bound fluid volume. For example, it has been observed that some mature, dewatered shales have relaxation time components below 0.3 msec. Bitumen volumes are also considerably underestimated

by MR measurements. Then $\phi_{sub.D} > BFV$, even when there is no free fluid. Under these circumstances, Equation (9) will erroneously indicate the presence of substantial permeability.

Detailed Description Text (15):

In order to automatically detect formations in which permeability is likely to be overestimated, a Low BFV Flag can be computed as: $\#EQU8\#$ Here $FFI_{sup.(-)}$ is the underestimated value of free fluid volume. FFI is underestimated in reduced cycle time logging because short wait times result in partial polarization of fluid components having $T_{sub.1} > W$. ϵ is a small constant (typically 0.25 p.u.) which prevents the denominator from going to zero in tight zones and shales.

Detailed Description Text (16):

The flag is zero in tight zones and in typical shales. In these zones, no correction to the computed permeability is required. In most other formations; $\phi_{sub.D} - BFV \approx FFI_{sup.(-)}$, so the Flag is near unity, which is denoted "low"; no correction to the computed permeability is required. In dewatered shales and bitumen, $\phi_{sub.D} - BFV > 0$ and $FFI_{sup.(-)} = 0$, so the Flag is high. In these zones the permeability can be automatically set equal to an arbitrarily low value. A flow diagram for this processing is described in conjunction with FIG. 9 below.

Detailed Description Text (17):

Oils of different viscosities have different nuclear magnetic resonance relaxation times [see Kleinberg, R. L. Vinegar, H. J., 1996, "NMR Properties of Reservoir Fluids", Log Analyst November-December 1996. pg. 20-32]. $T_{sub.2}$ distributions from the type of MR logging device described herein are routinely used to determine the viscosity, η , of oil in place, and to distinguish productive oil zones from heavy and immobile hydrocarbons, such as in tar mats. Moreover, oil-water contacts in wells drilled with water base mud can frequently be unambiguously identified using $T_{sub.2}$ measurements [see White, J., 1997, "Applications of Downhole Magnetic Resonance Imaging in the North Sea", Society of Petroleum Engineers Offshore Europe Conference Paper 38551].

Detailed Description Text (18):

Finding the oil-water contact (OWC) poses a challenge to magnetic resonance well logging when the well is drilled with oil base mud and the formation oil is light. In the water leg, oil base mud (OBM) filtrate displaces movable water in the volume of investigation of the MR tool, while in the oil leg, the filtrate mixes with formation oil. Because the nuclear magnetic resonance $T_{sub.2}$ is relatively insensitive to viscosity when $\eta < 1$ cP, the $T_{sub.2}$ distribution often shows no change at the OWC.

Detailed Description Text (19):

However, $T_{sub.1}$ remains sensitive to viscosity over the entire range of crudes and mud filtrates, as shown in FIG. 11 of Kleinberg, R. L. Vinegar, H. J., 1996, "NMR Properties of Reservoir Fluids", Log Analyst November-December 1996. pg. 20-32. Thus, $T_{sub.1}$ can be used to discriminate OBM filtrate from formation oil. The apparent NMR porosity $\phi_{sub.app}$ is the sum of contributions from the fluids in the formation. For true porosity ϕ and saturations $S_{sub.j}$ $\#EQU9\#$ where W is the wait time and $T_{sub.1j}$ is the relaxation time of fluid j . If the wait time is substantially longer than the $T_{sub.1}$'s of all fluids, $\phi_{sub.app} = \phi$, so the magnetic resonance signal amplitude will be unchanged as the tool crosses the OWC. On the other hand, reduced wait times can result in substantial signal amplitude changes. When combined with other porosity logs, use of a single MR pass will differentiate OBM-invaded water and oil zones.

Detailed Description Text (20):

FIG. 7 illustrates a basis of the technique. The factor in square brackets in Equation (11) is plotted versus $T_{sub.1}$ for three wait times: 8 sec, 1.3 sec, and 0.45 sec. Even 8 sec is not adequate to fully polarize fluids with $T_{sub.1} > 2$ sec, which includes many OBM filtrates and light oils. Using any of the three wait times will produce amplitude contrast between fluids of differing $T_{sub.1}$. While $W=0.45$ sec is shorter than optimal for the OWC application, this aggressively reduced wait time permits faster logging, improved vertical resolution and/or increased data stacking over the entire logged section while yielding good amplitude contrast at the OWC.

Detailed Description Text (21):

Referring to FIG. 8, there is shown a flow diagram of a routine for controlling a

processor in accordance with an embodiment of the invention. The processor can be a downhole processor, the uphole processor in equipment 7 (FIG. 1), or a remote processor which operates subsequently on stored and/or transmitted log-representative signals, as well as combinations of downhole, uphole, and remote processors. In the flow diagram of FIG. 8, the block 805 represents selecting of the wait time W . The wait time will be relatively short for incomplete polarization. The preferred range of W is 0.1 to 1 second. Next, as represented by the block 815, the echo spacing, TE , and the number of echoes are selected for the pulse sequence. The pulse sequence is then applied and the resultant echo train is recorded. It will be understood that any suitable technique can be used for applying the pulse sequence, a CPMG pulse sequence being used for the present embodiment. A $T_{sub.2}$ distribution is then generated from the echo train data, as represented by the block 840, and a standard free/bound fluid cutoff is developed, as represented by the block 850. Reference can be made, for example, to Straley, C., Rossini, D., Vinegar, H., Tutunjian, P., Morriss, C., 1997, "Core Analysis by Low Field NMR", Log Analyst, March-April 1997, pg. 84-94. The block 860 represents application of correction to the free fluid components of the $T_{sub.2}$ distribution, which are affected by the incomplete polarization, as previously described. In the present embodiment, the correction is in accordance with Equation (6). The density (or neutron-density) porosity, such as measured by device 60 (FIG. 1) is indicated as being available (block 1055), and can be utilized in a water zone to select the correction such that corrected MR porosity will match the total porosity $\phi_{T.sub.2}$ in the water zone flushed with oil base mud filtrate. The decision block 870 represents the comparison of the magnetic resonance porosity with the total porosity in an oil bearing zone. In a zone of light hydrocarbons, the MR porosity will be less than the neutron-density derived total porosity (since the applied correction will be too small), whereas in a zone of heavy oil the MR porosity will be greater than the neutron-density derived total porosity (since the applied correction will be too large). The block 875 represents the determination of residual oil saturation, which can be implemented e.g. by quantification of the comparison. Reference can be made to equation (A-10) below and the derivation thereof. The block 880 represents determination of permeability, e.g. by using Equation (9).

Detailed Description Text (22):

FIG. 9 is a flow diagram of a routine for programming a processor in accordance with an embodiment of the invention for producing and using the Flag for determining potentially overestimated permeability in certain formations wherein at least some of the bound water is not "seen" by the MR logging technique. Again, the processor can be a downhole, uphole, or remote processor. The blocks 805 through 850 (only block 850 being shown in FIG. 9) can correspond to their counterparts in the flow diagram of FIG. 8, with a short wait time again being used. After the free/bound

Detailed Description Text (23):

fluid cutoff is developed (block 850), the volumes of bound fluid (BFV) and free fluid (FFI_{sup.}(-)), which, as noted above, is the uncorrected and possibly underestimated volume of free fluid) are computed from the respective components of the $T_{sub.2}$ distribution (block 910). Using the computed values, and the porosity from block 855, the Flag can be computed (block 920). Determination is then made (decision block 930) as to whether the Flag is above a predetermined threshold. If so, the zone can be marked as one of potentially overestimated permeability (block 940).

Detailed Description Text (25):

In examples hereof, reduced cycle time logging is employed. The reservoirs of the examples were drilled with oil base mud and logged using an MR logging tool of the type described herein (and designated as the "CMR", which is a mark of Schlumberger) and other logging devices as in FIG. 1. [Regarding the CMR tool and processing, reference can be made to U.S. Pat. Nos. 5,055,787 and 5,291,137 and to Freedman, R., Morriss, C. E., 1995, "Processing of Data from an NMR Logging Tool", Society of Petroleum Engineers Paper 30560.] Log Example #1 was a well in the Andrew field in the North Sea. A logging objective was to acquire data at high speed and with enhanced vertical resolution. Neutron, density, resistivity and gamma ray logs were also run. Using the CMR tool to find yet another porosity measure is inefficient because formation oil and oil base mud filtrate both have long $T_{sub.1}$, so very slow logging would have been required. Even so, detailed log analysis shows that comparing reduced-cycle-time CMR apparent porosity to neutron-density porosity allows precise determination of the residual oil contact. The CMR logging device and pulse sequence parameters were (with SI being sampling interval):

Detailed Description Text (26):

The porosity analysis is as follows: The porosity logs are shown in FIGS. 10A and 10B, track 3. Density and neutron tools were used to determine porosity assuming a sandstone matrix and a fluid density of 0.9 g/cc. Log porosity is

Detailed Description Text (27):

The second term comes into play only in the presence of gas, where $\phi_{D} < \phi_{N}$. This porosity is in excellent agreement with core measurements, shown as dots. Water volume, $\phi_{S.W}$ is derived from deep resistivity (90 inch array). $R_{W} = 0.07$ $\Omega\text{-m}$ was selected so that resistivity-derived porosity matched crossplot porosity in the water leg below x760 feet: ##EQU10##

Detailed Description Text (28):

Porosity derived from the CMR tool is also shown, as is the T_{2} distribution from 0.3 msec to 3000 msec. The wait time of 0.45 sec was insufficient to fully polarize the native oil or oil base mud filtrate. Therefore the standard polarization correction was turned off and a fixed value of $T_{1} = 2.5$ sec was used in a custom polarization correction using Equation (6). This correction was applied only to the free fluid part of the signal. The value of T_{1} was picked so that the corrected CMR porosity matched the density porosity in the water leg (flushed with oil base mud filtrate) below x760. The excellent correlation can be noted.

Detailed Description Text (29):

The bound fluid volume, BFV, is shown in Track 3. The formation is a very clean sand, in which there is little bound water. The $T_{2\text{cutoff}} = 100$ msec was selected so that BFV matched $\phi_{S.W}$ high in the hydrocarbon zone. The one parameter fit of CMR data yields excellent curve-character agreement with irreducible water volume determined by resistivity above the transition zone, FIG. 10, Track 3. A conventional sharp cutoff was used. The use of a tapered cutoff [see Coates, G. R., Marschall, D., Mardon, D., Galford, J., 1997, "A New Characterization of Bulk Volume Irreducible Using Magnetic Resonance", SPWLA 38th Annual Logging Symposium, Paper QQ; Kleinberg, R. L., Boyd, A., 1997, "Tapered Cutoffs for Magnetic Resonance Bound Water Volume", Society of Petroleum Engineers Paper 38737] would not be appropriate here, because most of the CMR signal is from the non-wetting phase (oil and oil base mud filtrate) and therefore is not reflective of the pore size distribution of the rock.

Detailed Description Text (30):

In the hydrocarbon analysis, the CMR log, combined with other logs, reveals five distinct zones (FIG. 10). (1) Below x760 the sand is water saturated; oil base mud filtrate has displaced water in the CMR tool volume of investigation. (2) The original ("paleo") oil-water contact is marked by heavy oil bands at x760 and x750. (3) A layer of dead residual oil, remaining after partial depletion of the reservoir, is found between x740 and x705. (4) Live crude (mixed with OBM filtrate in the flushed zone) is found between x705 and x530. (5) Gas mixed with OBM filtrate is found above x530.

Detailed Description Text (31):

In the water sand, the free fluid is oil base mud filtrate which has displaced movable connate water. OBM filtrates are often alkanes of moderate chain length (e.g. hexadecane, C16), and lack dissolved gas. As explained above, porosity from the CMR tool matches nuclear porosity in this interval when $T_{1} = 2.5$ sec is used in the polarization correction.

Detailed Description Text (32):

When formation crude has a viscosity greater than OBM filtrate, the polarization correction used to match CMR porosity to nuclear porosity below the oil-water contact will be too large. The overcorrection will make CMR porosity larger than nuclear porosity. This is observed in streaks at x760 and x750, where polarization corrected CMR porosity (dashed line) is higher than nuclear porosity (heavy solid line). The presence of heavy oil is sometimes associated with the original oil-water contact in North Sea reservoirs, and is confirmed by the operator in this example.

Detailed Description Text (33):

Above the paleo OWC, from x740 to x705, is a depleted zone in which formation oil has been stripped of gas and light ends. The dead oil here, mixed with mud filtrate, appears to have magnetic resonance properties similar to those of the unmixed filtrate below x760. The polarization correction using $T_{1} = 2.5$ sec again

perfectly matches CMR porosity to nuclear and core porosities.

Detailed Description Text (34):

CMR porosity departs from the other porosity measurements above x705 feet. This is interpreted as the depth at which there is the first appearance of live oil in the CMR volume of investigation. This is the native formation oil, composed of short chain alkanes, and having a significant amount of dissolved gas. Its viscosity at reservoir conditions is 0.29 cP. The low viscosity of live formation crude means its relaxation time is significantly longer than that of dead crude and OBM filtrate. When live native oil is present, $T_{sub.1} = 2.5$ sec is no longer large enough to provide an adequate polarization correction, and CMR porosity is too low.

Detailed Description Text (35):

Resistivity shows a very long transition zone spanning more than 80 feet, a consequence of the rock fabric: small pore throats trap formation water at high capillary pressure. However, because there is no capillary pressure difference between OBM filtrate, dead oil, and live oil, the current fluid contact detected by CMR at x705 is sharp. Volumetric analysis is shown in Track 1. Total hydrocarbon saturation is determined by deep resistivity. The live oil volume is found from CMR data; the method by which it is determined being set forth in the Appendix below.

Detailed Description Text (36):

Neutron-density crossover indicates gas above x530. Native gas has mixed with the dead OBM filtrate, producing a mixture with a reduced viscosity and therefore long $T_{sub.1}$. This effect can be helpful in finding gas-oil contacts, but hydrogen index effects and variability in the degree of mixing make it difficult to quantitatively estimate volumes.

Detailed Description Text (37):

Permeability was estimated by $\#EQU11\#$ where ϕ is the Equation (12) porosity and BFV is the CMR bound fluid volume. The first term is the Equation (9) permeability. The second term is a permeability function appropriate for clean sands [see Herron, M. M., 1987, "Estimating the Intrinsic Permeability of Clastic Sediments from Geochemical Data", SPWLA 28th Annual Logging Symposium, Paper HH]. The permeability was set to 0.01 mD whenever the permeability flag of Equation (10) exceeded 4 with $\epsilon = 0.25$ p.u. Agreement with core permeability is good, within the limitations of depth matching and resolution (FIG. 10, Track 2).

Detailed Description Text (39):

Reduced wait time MR logging was used in a second field on the UK continental shelf to enhance logging speed and measurement precision. Oil base mud was used to drill into a shaly sand light oil reservoir. Conventional porosity tools were used for porosity and lithology determination, as above. Porosity was computed as for Log Example #1, using a fluid density of 0.8 g/cc, appropriate for the oil base mud filtrate in this well. CMR logging obtained measurements of bound water and permeability. The formation of interest was logged with two passes of the CMR. Logging and pulse sequence parameters were (with S=PAP's stacked per 6 inch depth frame)

Detailed Description Text (40):

The first pass was designed to obtain a full suite of MR measurements, including porosity and free fluid porosity. The second pass was designed to determine the quality of CMR logs acquired at higher speed, where measurement precision was an important consideration. Porosity and $T_{sub.2}$ distribution were derived from the CMR tool.

Detailed Description Text (41):

For the slow pass, the standard polarization correction was applied using $T_{sub.1} / T_{sub.2} = 3$, which is typical for formations invaded with oil base mud filtrates. For the fast pass, less than 0.1 sec of data are collected in each CPMG acquisition. Therefore, the longer $T_{sub.2}$ components in the $T_{sub.2}$ distribution cannot be accurately estimated. This leads to errors when the conventional polarization correction method, based on the $T_{sub.1} / T_{sub.2}$ ratio, is applied. Therefore $T_{sub.1} = 0.5$ sec was assumed for the mud filtrate, and a fixed $T_{sub.1}$ correction applied to the free fluid part of the measured porosity. $T_{sub.1}$ of the bound fluid is much shorter, and no polarization correction is required.

Detailed Description Text (42):

The hydrogen index of the OBM filtrate was determined by obtaining a sample of the

base oil used to make up the whole mud. In the shop, the CMR was used to compare the amplitude of the signal from the base oil to an identical volume of the aqueous master calibration solution. The hydrogen index was found to be 0.83, a surprisingly low value. This correction was applied to the free fluid component; the bound fluid is formation water, with HI=1. It was assumed that the neutron tool, which has a significantly deeper depth of investigation, was substantially unaffected by the low HI of the filtrate. The measured mud filtrate density, used for bulk density computation of porosity, was 0.8 g/cc. The logs are shown in FIG. 11.

Detailed Description Text (43):

In the slow pass analysis, a wait time of 4 sec was employed to substantially polarize the oil base mud filtrate which partially displaced the connate free fluid in the flushed zone. 1800 echoes were collected to define the long T_{sub.2} components associated with OBM filtrates. One phase alternated pair (PAP) was collected in each 6 inch depth frame.

Detailed Description Text (44):

Total CMR porosity matches density porosity. The T_{sub.2} distribution in the shales (Track 3) is generally well resolved and is centered around 3 msec. Note several permeable streaks, for example at x734 meters, indicated by high amplitude at long T_{sub.2}.

Detailed Description Text (45):

In the sand, x678-x705 meters, CMR shows that reservoir quality varies with depth. Bound fluid volume (BFV), the amplitude below T_{sub.2}-cutoff =33 msec, correlates with gamma ray, which has been plotted on a scale of 30 to 110 API units to emphasize the similarity of the curves (Track 1). The correlation coefficient (from the MatLab function "corrcoef") is 0.80 over the entire section shown.

Detailed Description Text (46):

In the fast pass analysis the goals were to achieve both better precision in bound fluid volume and enhanced logging speed. A 0.25 sec wait time and acquisition of only 300 echoes permitted a logging speed of 600 ft/hr, with four phase alternated pairs stacked per 6 inch depth frame. Thus, the effective signal to noise ratio was doubled while the logging speed was improved by a factor of three, compared to the conventional pass.

Detailed Description Text (47):

In the shales, the fast pass results correlate well with those of the slow pass; free fluid near zero, CMR total porosity in excellent agreement with density porosity, and good correlation between bound fluid-volume and gamma ray. The T_{sub.2} distributions for the two runs are similar below 33 msec; the fast pass results (Track 4) are more stable due to superior signal to noise ratio.

Detailed Description Text (48):

In the sands, the fast pass suppressed long relaxation time components and moved them to somewhat shorter T_{sub.2}, but the use of a polarization correction (T_{sub.1} =0.5 sec) restored free and total CMR porosity (Tracks 2 and 4). The correction is large and distorts the T_{sub.2} distribution, but excellent agreement between fast and slow pass porosity demonstrates that the polarization correction is accurate, and that no long-T_{sub.1} components are unaccounted for.

Detailed Description Text (49):

As expected, the fast pass improved the definition of the bound fluid in the T_{sub.2} distributions. The improved signal to noise ratio of the fast pass manifests itself in visibly improved correlation between BFV and gamma ray. This conclusion is supported by statistical examination. The correlation coefficient is 0.91.

Detailed Description Text (53):

Residual oil saturation in Well #1 was determined by comparing the partially polarization-corrected CMR porosity to total porosity determined from density and neutron tools. The wait time W=0.45 sec. At the CMR depth of investigation, the water leg is saturated with irreducible water, oil base mud filtrate, and dead residual oil. The irreducible water has very short T_{sub.1}, and no polarization correction was applied to it. The T_{sub.1}'s of the OBM filtrate and dead crude were assumed equal and were determined by applying the polarization correction, Equation (6), to the free fluid to match CMR porosity to nuclear porosity in the water leg; a value of T_{sub.1}dead =2.5 sec was found.

Detailed Description Text (54):

The oil leg contains irreducible water, oil base mud filtrate, and live native hydrocarbon. This mixture, which is rich in gas and has a viscosity at reservoir conditions of $\eta = 0.29$ cP, Longitudinal relaxation time is estimated by ##EQU13## giving approximately $T_{sub.1live} = 6$ sec at reservoir temperature.

Detailed Description Text (55):

The uncorrected CMR signal is ##EQU14## For wait time $W = 0.45$ sec, and $T_{sub.1}$ for mud filtrate and oil as given in the table,

Detailed Description Text (56):

The polarization corrected CMR signal is ##EQU15## where $FFI_{sup.(-)}$ is the apparent free fluid volume, which is less than its true value due to insufficient wait time. Assuming the bound fluid volume and the water volume are the same, the free fluid is corrected by

Detailed Description Text (60):

Solving (A-8) for the volume of live oil

Detailed Description Paragraph Equation (1):

$k = a \cdot \phi_{sup.4} T_{sup.2} \log(7)$ ##EQU6## The constants a and a' are formation dependent, with default values $a = 4$ mD/msec.² and $a' = 10$ mD.⁴ The use of Equation (7) calls for a porosity measurement and computation of the logarithmic mean of the entire $T_{sub.2}$ distribution, while the use of Equation (8) calls for measurements of porosity ϕ , bound fluid volume BFV, and free fluid volume FFI. Thus, both relationships ostensibly require the measurement of the full nuclear magnetic resonance $T_{sub.2}$ distribution, necessitating a long measurement cycle time.

Detailed Description Paragraph Table (3):

| | |
|--|--|
| | Fluid Volume $T_{sub.1}$ (sec) |
| | Irreducible <u>water</u> $V_{sub.W} < 0.45$ Filtrate + |
| Dead Residual $V_{sub.dead} T_{sub.1dead} =$ | 2.5 Live <u>Oil</u> $V_{sub.live} T_{sub.1live} = 6$ |

Other Reference Publication (1):

Meiboom, S., Gill, D., 1958, "Modified Spin Echo Method for Measuring Nuclear Relaxation Times", Review of Scientific Instruments, 29, 688-691.

Other Reference Publication (2):

Sezginer, A., Kleinberg, R.L., Fukuhara, M., Latour, L.L., 1991, "Very Rapid Simultaneous Measurement of Nuclear Magnetic Resonance Spin-Lattice Relaxation Time and Spin-Spin Relaxation Time", Journal of Magnetic Resonance 92, 504-527.

Other Reference Publication (3):

Kleinberg, R.L. Vinegar, H.J., 1996, "NMR Properties of Reservoir Fluids", Log Analyst Nov.-Dec. 1996. p. 20-32.

Other Reference Publication (4):

Morriss, C.E., Deutch, P., Freedman, R., McKeon, D., Kleinberg, R.L., 1996., "Operating Guide for the Combinable Magnetic Resonance Tool", Log Analyst, Nov.-Dec. 1996, p. 53-60.

Other Reference Publication (5):

Straley, C., Rossini, D, Vinegar, H., Tutunjian, P., Morriss, C., 1997, "Core Analysis by Low Field NMR", Log Analyst, Mar.-Apr. 1997, p. 84-94.

Other Reference Publication (6):

Kleinberg, R.L., Straley, C., Kenyon, W.E., Akkurt, R., Farooqui, S.A., 1993, "Nuclear Magnetic Resonance of Rocks: $T_{sub.1}$ vs. $T_{sub.2}$ ", Society of Petroleum Engineers Papers 26470.

Other Reference Publication (7):

Straley, C., Morriss, C.E., Kenyon, W.E., Howard, J.J., 1995, "NMR in Partially Saturated Rocks", Log Analyst, Jan.-Feb. 1995, p. 40-56.

Other Reference Publication (8):

Singer, J.M., Johnston, L., Kleinberg, R.L., Flaum, C., 1997, "Fast NMR Logging for Bound Fluid and Permeability", SPWLA 38th Annual Logging Symposium, Paper YY.

Other Reference Publication (9):

Prammer, M.G., Drack, E.D., Bouton, J.C., Gardner, J.S., 1996, "Measurements of Clay Bound Water and Total Porosity by Magnetic Resonance Logging", Long Analyst, Nov.-Dec. 1996, p. 61-69.

Other Reference Publication (10):

Freedman, R., Boyd, A., Gubelin, G., McKeon, D., Morriss, C.E., Flaum C., 1997, "Measurement of Total NMR Porosity Adds New Value to NMR Logging", SPWLA 38th Annual Logging Symposium, Paper 00.

Other Reference Publication (11):

Kenyon, B., Kleinberg, R., Straley, C., Gubelin, G., Morriss, C., 1995, "Nuclear Magnetic Resonance--Technology for the 21st Century", Schlumberger Oilfield Review, Autumn 1995, p. 19-33.

Other Reference Publication (12):

White, J., 1997, "Applications of Downhole Magnetic Resonance Imaging in the North Sea", Society of Petroleum Engineers Offshore Europe Conference Paper 38551.

Other Reference Publication (13):

Murphy, D.P., 1995, "NMR Logging and Core Analysis Simplified", World Oil, Apr. 1995, p. 65-70.

Other Reference Publication (14):

Freedman, R., Morriss, C.E., 1995, "Processing of Data from an NMR Logging Tool", Society of Petroleum Engineers Paper 30560.

Other Reference Publication (15):

Coates, G.R., Marschall, D., Mardon, D., Galford, J., 1997, "A New Characterization of Bulk Volume Irreducible Using Magnetic Resonance", SPWLA 38th Annual Logging Symposium, Paper QQ.

Other Reference Publication (16):

Kleinberg, R.L., Boyd, A., 1997, "Tapered Cutoffs for Magnetic Resonance Bound Water Volume", Society of Petroleum Engineers Paper 38737.

CLAIMS:

1. A method for determining residual oil saturation in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W, of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes to obtain a magnetic resonance porosity;

deriving a measure of total porosity of said formations; and

determining residual oil saturation from said magnetic resonance porosity and said total porosity.

4. The method as defined by claim 1, further comprising applying a polarization correction to said magnetic resonance porosity from said T_{sub.2} distribution.

5. The method as defined by claim 1, wherein said step of processing the received spin echoes to obtain a magnetic resonance porosity includes processing the received spin echoes to produce a T_{sub.2} distribution, and computing said magnetic resonance porosity from said T_{sub.2} distribution.

6. The method as defined by claim 5, further comprising applying a polarization correction to the free fluid components of said T_{sub.2} distribution before computing said magnetic resonance porosity from said T_{sub.2} distribution.

7. The method as defined by claim 6, wherein said polarization correction is of the form $P(T_{sub.2i})$ where $P(T_{sub.2i})$ is the corrected $T_{sub.2}$ distribution, $P(T_{sub.2i}).sub.uncorr$ is the uncorrected $T_{sub.2}$ distribution, and $T_{sub.1}$ is a selected longitudinal relaxation time of the free fluid.

8. The method as defined by claim 5, further comprising the steps of developing a free/bound fluid cutoff of said $T_{sub.2}$ distribution and applying a polarization correction to the free fluid components of said $T_{sub.2}$ distribution before computing said magnetic resonance porosity from said $T_{sub.2}$ distribution, and wherein said step of determining residual oil saturation from said magnetic resonance porosity and said total porosity comprises comparing said respective porosities in a water-bearing zone of said formations and comparing said respective porosities in an oil-bearing zone of said formations.

9. A method for determining an indication that a formation surrounding an earth borehole has a potentially overestimated permeability, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes and deriving a bound fluid volume, BFV , and a free fluid volume $FFI_{sup}(-)$ from said received spin echoes;

deriving a measure of total porosity ϕ of said formations; and

deriving a flag indicative of potentially overestimated permeability from said BRV , $FFI_{sup}(-)$, and ϕ .

13. Apparatus for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising: a nuclear magnetic resonance logging device that is moveable through the borehole;

means, in said logging device, for providing a polarizing magnetic field and cycles of a magnetic pulse sequence, and for receiving magnetic resonance spin echoes from the formations;

means for processing the received spin echoes to obtain a magnetic resonance porosity;

means for deriving a measure of total porosity of said formations; and

means for comparing said magnetic resonance porosity with said total porosity, said comparing means comprising means for comparing said respective porosities in a water-bearing zone of said formations and for comparing said respective porosities in an oil-bearing zone of said formations.

15. Apparatus as defined by 14, further comprising means for determining the residual oil saturation of said formations from the output of said comparing means.

16. Apparatus for determining residual oil saturation in formations surrounding an earth borehole, comprising:

a nuclear magnetic resonance logging device that is moveable through the borehole;

means, in from said logging device, for providing a polarizing magnetic field and cycles of a magnetic pulse sequence, and for receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

means for processing the received spin echoes to obtain a magnetic resonance porosity;

means for deriving a measure of total porosity of said formations; and

means for determining residual oil saturation from said magnetic resonance porosity and said total porosity.

17. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes to obtain a magnetic resonance porosity;

deriving a measure of total porosity of said formations from a density and/or neutron porosity measurement in said investigation region of the formations; and

comparing said magnetic resonance porosity with said total porosity.

19. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations;

processing the received spin echoes to obtain a magnetic resonance porosity;

deriving a measure of total porosity of said formations; and

comparing said magnetic resonance porosity with said total porosity, said comparing step comprising comparing said respective porosities in a water-bearing zone of said formations and comparing said respective porosities in an oil-bearing zone of said formations.

22. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes to obtain a magnetic resonance porosity by processing the received spin echoes to produce a $T_{sub.2}$ distribution, applying a polarization correction to the free fluid components of said $T_{sub.2}$ distribution, said polarization correction being of the form $##EQU19##$ where $P(T_{sub.2i})$ is the corrected $T_{sub.2}$ distribution, $P(T_{sub.2i}).sub.uncorr$ is the uncorrected $T_{sub.2}$ distribution, and $T_{sub.1}$ is a selected longitudinal relaxation time of the free fluid, and computing said magnetic resonance porosity from said polarization corrected $T_{sub.2}$ distribution;

deriving a measure of total porosity of said formations; and

comparing said magnetic resonance porosity with said total porosity.

23. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence being short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes to obtain a magnetic resonance porosity by processing the received spin echoes to produce a $T_{sub.2}$ distribution, developing a free/bound fluid cutoff of said $T_{sub.2}$ distribution, applying a polarization correction to the free fluid components of said $T_{sub.2}$ distribution, and computing said magnetic resonance porosity from said $T_{sub.2}$ distribution;

deriving a measure of total porosity of said formations; and

comparing said magnetic resonance porosity with said total porosity, said comparing step comprising comparing said respective porosities in a water-bearing zone of said formations and comparing said respective porosities in an oil-bearing zone of said formations.

24. The method as defined by claim 23, wherein said earth borehole was drilled with oil base mud, and wherein said step of comparing said magnetic resonance porosity with said total porosity comprises comparing said respective porosities in a water-bearing zone of said formations that has been flushed with oil base mud filtrate and comparing said respective porosities in an oil-bearing zone of said formations.

25. The method as defined by claim 24, further comprising the step of identifying the presence of light oil in said formations when the corrected magnetic resonance porosity is less than the total porosity.

26. The method as defined by claim 24, further comprising the step of identifying the presence of heavy oil in said formations when the corrected magnetic resonance porosity is greater than the total porosity.

27. The method as defined by claim 23, further comprising the step of identifying the presence of light oil in said formations when the corrected magnetic resonance porosity is less than the total porosity.

28. The method as defined by claim 23, further comprising the step of identifying the presence of heavy oil in said formations when the corrected magnetic resonance porosity is greater than the total porosity.

29. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole that has been drilled with oil base mud, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations;

processing the received spin echoes to obtain a magnetic resonance porosity;

deriving a measure of total porosity of said formations; and

comparing said magnetic resonance porosity with said total porosity.

31. The method as defined by claim 29, further comprising the step of computing the residual oil saturation of said formations as a function of said comparison.

32. A method for identifying characteristics of hydrocarbons in formations surrounding an earth borehole, comprising the steps of:

providing a nuclear magnetic resonance logging device that is moveable through the borehole;

providing, from said logging device, a polarizing magnetic field and cycles of a magnetic pulse sequence, and receiving magnetic resonance spin echoes from the formations, the polarization wait time, W , of said cycles of magnetic pulse sequence is short enough to incompletely polarize the protons in an investigation region of the formations;

processing the received spin echoes to obtain a magnetic resonance porosity;

deriving a measure of total porosity of said formations; and

comparing said magnetic resonance porosity with said total porosity and computing the residual oil saturation of said formations as a function of said comparison.



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File: USPT

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TITLE: Permeability determination from NMR relaxation measurements for fluids in porous mediaAbstract Text (1):

The present invention is a method to rapidly determine the fluid-flow permeability of porous media with nuclear magnetic resonance (NMR). The method can be applied to measurements of permeability in fluid-saturated earth formations using NMR logging tools.

Inventor City (1):

High Bridge

Inventor Group (1):

Jerosch-Herold; Michael High Bridge NJ

Brief Summary Text (2):

The present invention relates to a method for determining the fluid flow permeability of porous media. In particular, the present invention relates to measuring the permeability by nuclear magnetic resonance (NMR) using the T_{sub 2} relaxation time for the decay of the transverse magnetization of fluids saturating the medium under investigation.

Brief Summary Text (3):

The properties of fluid in porous media are of great relevance in many fields of science and engineering. There are numerous measurements which bear some importance on characterizing fluid properties in confined geometries like sandstone rocks. We list here a few: porosity, fluid flow permeability (both dc and ac), electrical conductivity, wettability, etc. Quantities like porosity and fluid flow permeability in porous rocks are of great relevance for determining, the producibility of petroleum reservoirs.

Brief Summary Text (4):

For porous media it has become customary to speak of the solid material which forms the "backbone" as the matrix and its complement as the pore space. Porosity is defined as the ratio of pore space volume inside the porous material to the total volume of the porous medium. Permeability is a measure for the ability of porous materials like e.g. porous rocks to permit fluid flow through the pore space. It generally increases with porosity, but also depends on other parameters of the rocks as e.g. the specific surface area of the pore space, the pore size distribution and the pore shape. The fluid flow permeability can vary by about 8 orders of magnitude in loose sediments and sedimentary rocks. It has the dimension of area and is defined by Darcy's law which relates the rate of fluid flow to the pressure differential between two parallel planes for inflow and outflow. The fluid flow permeability is measured in the laboratory by fitting sleeves to core samples which are often cylindrically shaped. The top and bottom of the core samples are connected to fluid inlets and outlets and a known pressure difference is applied across the sample. The fluid flow rate is measured for a set of different pressure gradient. Liquids or gases can be used as flowing medium, although the measurement using a liquid is generally easier as in most cases the liquid can be considered incompressible. The laboratory procedure therefore requires first to drill core plugs from core samples, which have to be cleaned with various solvents. In contrast the method of the present invention can be carried out with a nuclear magnetic resonance logging tool to measure in situ the transverse relaxation time of the fluids saturating an earth formation to accurately predict the fluid flow

permeability of the earth formation.

Brief Summary Text (5):

Nuclear magnetic resonance (NMR) has been employed for some time to study fluids permeating the pore space of porous media [see J. R. Banavar and L. M. Schwartz, "Molecular Dynamics in Restricted Geometries", chapter 10, edited by J. Klafter and J. M. Drake, J. Wiley (1989)]. The fluid supplies the probe particles which diffuse in the pore space. Since the classic paper by Brownstein and Tarr (BT) [see K. R. Brownstein and C. E. Tarr, Physical Review A, 19, 2446(1979)] it has been realized that nuclear spin relaxation can provide information about the pore space geometry. BT discussed the case of $T_{sub.1}$ and $T_{sub.2}$ relaxation in an isolated pore where the nuclear spins are relaxed by collisions with the pore walls. The interpretation of $T_{sub.1}$ measurements with this model for fluids in porous media can present several problems. In the limit where the nuclear spins diffuse at a fast rate to the pore surface and the surface relaxation is in comparison relatively slow, the averaged relaxation curve can be related to the pore size probability distribution. In this so called fast diffusion limit where the lowest order relaxation mode dominates one still has to assume that the surface relaxation strength is uniform and the pores are isolated to relate the distribution of relaxation times uniquely to the pore size distribution. It is conceivable to have porous samples with the same pore size geometry but different levels of paramagnetic impurities which influence the surface relaxation velocity while the fluid flow permeability would remain unchanged. To obtain a reliable estimate of the fluid flow permeability with NMR one therefore has to perform an experiment which directly probes fluid transport in the porous medium like for example the diffusion of fluid molecules in the pore space. For $T_{sub.1}$ measurements the nuclear spin relaxation depends on the rate at which magnetization is carried to the surface but also on the surface relaxation velocity ρ . As the surface relaxation strength ρ has no bearing on permeability one can therefore hope to correlate $T_{sub.1}$ and the fluid flow permeability only for classes of materials with similar surface relaxation properties.

Brief Summary Text (6):

There is an increasing interest in applying NMR in well-bore environments to determine the properties of fluid carrying earth formations [see P. N. Sen, C. Straley, W. E. Kenyon and M. S. Whittingham, Geophysics, 55, 61-69(1990)]. This interest has been spurred by the introduction of a new generation of NMR logging tools by NUMAR [see M. N. Miller, A. Paltiel, M. E. Gillen, J. Granot and J. C. Brouton, Society of Petroleum Engineers, SPE 20561, 321(1990)], which are already being used in the field. The new NMR logging tools are very well fitted to carry out the physical-measurements required for our method of invention.

Brief Summary Text (7):

In the present invention, a measurement of the transverse relaxation time $T_{sub.2}$ for fluids in porous media is used to determine the permeability of the medium by taking advantage of magnetic field inhomogeneities across pores. For strong magnetic fields and in the fast diffusion limit the relaxation is determined to first order by the transport of magnetization through the pore space and not the surface relaxation velocity. It will be shown that it is possible to correlate $T_{sub.2}$ to a length characteristic of the pore space geometry which can also be determined independently from mercury injection experiments and thereby relate $T_{sub.2}$ to the fluid flow permeability. It is also feasible to study the degree to which the diffusion of fluid molecules is restricted by the pore space geometry. $T_{sub.2}$ for fluids in porous media is in general orders of magnitude shorter than $T_{sub.1}$ in marked contrast to the situation for bulk fluids. The main mechanism for $T_{sub.2}$ relaxation of the fluid spins in strong magnetic fields is due to the internal random magnetic field gradients generated by the difference in magnetic susceptibility for the fluid filling the pore space and the material making up the matrix of the porous medium. At low fields surface relaxation can not be neglected but the τ dependence of $T_{sub.2}$ (τ) is still primarily due to diffusion in the internal magnetic field gradients. Surface relaxation will under standard experimental conditions not lead to a τ dependence of $T_{sub.2}$ in a CPMG experiment. This is confirmed by recent experimental results at low field with an NMR logging tool [see M. N. Miller, A. Paltiel, M. E. Gillen, J. Granot and J. C. Brouton, Society of Petroleum Engineers, SPE 20561, 321(1990)]. The spatial dependence of the internal gradients is determined by the pore space geometry and pore size distribution. The internal gradients in turn determine the rate at which the spins diffusing through the pore space lose their phase memory. The loss of phase memory can be monitored with a multi spin-echo pulse sequence like the

Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [see S. Meiboom and D. Gill, Rev. Sci. Instr., 29, 688 (1958)].

Brief Summary Text (8):

The phenomenon of spin echoes essential to the present invention was first discovered in NMR by Erwin Hahn [see E. L. Hahn, Phys. Rev., 77, 297 (1950)]. In an inhomogeneous magnetic field nuclear spins will precess at a Larmor frequency, ω , determined by the local field. After an initial radiofrequency pulse which tips the spins into a plane transverse to the direction of the applied static magnetic field the spins are all in phase and the sum of the total transverse magnetization is at the maximum possible value. Due to the spread in precession frequencies the spins will dephase and the macroscopic magnetization measured with the NMR instrument will decay. It is useful to remember here that the macroscopic magnetization is a vector sum of the magnetic moments of the spins which vanishes when the phases of the magnetic moments are random. One can reverse the dephasing process by applying a 180 degree pulse a time $\tau/2$ after the initial radio-frequency pulse which tipped the nuclear spins into the transverse plane. Immediately after this pulse a spin which precesses at a faster frequency than the average lags behind by an angle which is exactly the same angle by which it was ahead of the average immediately before the 180 degree pulse. Similarly spins precessing at a frequency slower than the average are now ahead. A time $\tau/2$ after the 180 degree pulse the spins will be again be in phase and one can observe a spin-echo. Spins diffusing will be subject to different local fields between the time the first pulse was applied and the detection of the spin echo. As their Larmor frequency is not constant the refocusing of magnetization will be incomplete and the echo will be attenuated. The degree of attenuation depends on the displacement and field inhomogeneity. This attenuation can be used to measure diffusion constants in fluids and to probe the diffusion of fluid spins in the pore space of porous media.

Brief Summary Text (10):

The present invention provides a method for determining the permeability of porous media saturated with a liquid using nuclear magnetic resonance (NMR). The steps of the method include: (a) applying a radiofrequency pulse sequence which after an initial pulse generates successive spin echoes with a train of radio frequency pulses spaced apart by a time interval of length τ , wherein all pulses have a carrier frequency corresponding to the Larmor frequency of the fluid spins filling the pore space of the medium for which the fluid flow permeability is to be determined; (b) measuring the decay of the transverse magnetization at each of the successive regularly spaced midpoints between the 180 degree pulses where the midpoints coincide with the peak of the spin echoes; (c) repeating steps a and b at least one more time wherein each repeat of step (a) uses said radio frequency pulse train with a different value of the pulse spacing τ ; (d) determining the transverse relaxation time $T_{sub 2}$ (τ), from the transverse magnetization decay for each value of τ , and determining one of a prefactor Δ , or a restricted diffusion length $l_{sub nmr}$ from said $T_{sub 2}$ (τ); (e) measuring the porosity of said porous media; (f) determining the permeability of said media from the porosity and either a prefactor Δ , or a restricted diffusion length $l_{sub nmr}$ from said $T_{sub 2}$ (τ).

Brief Summary Text (11):

In a preferred embodiment the method is performed as a down-hole wellbore measurement to swiftly and accurately determine the fluid-producing potential of an earth formation using a magnetic resonance logging system which employs static and radio-frequency magnetic fields to perform the spin-echo CPMG pulse experiment in a wellbore environment.

Drawing Description Text (3):

FIG. 1b shows the numerically evaluated CPMG decay for a certain τ value and the pore size distribution shown in (1a);

Drawing Description Text (4):

FIG. 1c shows the $T_{sub 2}$ values calculated from computer simulated CPMG decays for the same pore size distribution.

Drawing Description Text (5):

FIG. 2 shows a fit of $T_{sub 2}$ (τ) for a restricted diffusion model.

Drawing Description Text (7):

FIG. 4 shows the values of $T_{sub 2}$ (τ , $\tau_{fwdarw.0}$) obtained from numerical

calculations for a set of pore size distributions versus the width Δ of the pore size distribution.

Drawing Description Text (8):

FIG. 5: Schematic diagram of the NMR spin-echo pulse sequence used for the measurement of $T_{sub.2}$.

Drawing Description Text (9):

FIG. 6 shows an example of stretched exponential fit to CPMG decay for a water imbibed sandstone sample.

Drawing Description Text (10):

FIG. 7 shows the dependence of $T_{sub.2}$ on CPMG pulse spacing τ for a set of sandstone samples. The $T_{sub.2}$ values can be extrapolated to $T_{sub.2}(\tau \rightarrow 0)$ with an exponential function.

Drawing Description Text (11):

FIG. 8 shows a graph of extrapolated value of $T_{sub.2}$ versus $l_{sub.c}$ determined from mercury injection for sandstone rock samples.

Drawing Description Text (12):

FIG. 9 shows a graph of $T_{sub.2}(\tau \rightarrow 0) \cdot \phi$ (ϕ is the porosity) versus permeability k for sandstone rock samples.

Detailed Description Text (2):

The present invention is a method to determine the permeability of porous media using pulsed nuclear magnetic resonance. This method uses the relaxation decay of the transverse component of the magnetization ($T_{sub.2}$ relaxation) measured with the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence.

Detailed Description Text (4):

where $\beta_{sub.2}$ is the stretch exponent. A nonlinear least squares fit of the measured values of magnetization $m(t)$ to the stretched exponential function determines the relaxation time $T_{sub.2}$ and the stretch exponent, $\beta_{sub.2}$. If the pulse spacing, τ , is changed in incremental steps, a set of stretched exponential curves is produced yielding different values for $T_{sub.2}(\tau)$. For the case of free diffusion, the pore size distribution introduces a spectrum of $T_{sub.2}$ decay values because the internal magnetic field gradient is related to the pore size. The analysis of the transverse magnetization decay in this case yields an effective $T_{sub.2}$, which is a weighted average over the range of $T_{sub.2}$ values. In this case a characteristic length can be determined from the prefactor of the functional form that describes the τ dependence of $T_{sub.2}(\tau)$. When $T_{sub.2}$ is only measured for a limited range of τ values this prefactor is dominated by the pore size distribution and is not very sensitive to the exact functional form of $T_{sub.2}(\tau)$. A characteristic length, Δ , is derived from this prefactor.

Detailed Description Text (5):

where $F(\tau)$ is a fitting function which reproduces the τ dependence of $T_{sub.2}$. Specific forms for $F(\tau)$ are discussed in the section on Theoretical Background.

Detailed Description Text (6):

For a sufficiently wide range of τ values, the exact functional form of $T_{sub.2}(\tau)$ is determined by the cross-over from free to restricted diffusion. For a given range of τ values, this cross-over is also dependent on the pore size distribution. Analysis of the functional form of $T_{sub.2}(\tau)$ in the region of this cross-over yields a characteristic length, $l_{sub.nmr}$, according to: $l_{sub.nmr} = \Delta \sqrt{\tau / T_{sub.2}(\tau)}$. In either case, the characteristic lengths, Δ or $l_{sub.nmr}$, derived from the decay of $T_{sub.2}(\tau)$ with τ , are a measure of the fluid flow permeability. With $l_{sub.nmr}$ the fluid flow permeability is determined with

Detailed Description Text (7):

If a prefactor Δ has been determined from $T_{sub.2}(\tau)$ the fluid flow permeability is determined with:

Detailed Description Text (8):

If $T_{sub.2}(\tau)$ is a simple exponential then the prefactor Δ and the extrapolated value of $T_{sub.2}(\tau)$ are related by $T_{sub.2}(\tau \rightarrow 0) = \Delta \sqrt{\tau / T_{sub.2}(\tau)}$. The value of $T_{sub.2}$ extrapolated to $\tau \rightarrow 0$ combined with the

porosity, ϕ , of the material gives the permeability, k , of the porous medium according to (see FIG. 9):

Detailed Description Text (9):

The permeability relations 4, 5 and 6 follow from the relations: k varies. $1.\text{sub.c}.\text{sup.2} \phi.\text{sup.2}$ and Δ varies. $1.\text{sub.nmr}$ varies. $1.\text{sub.c}$ and $T.\text{sub.2}$ ($\tau.\text{fwd}.\text{arw.0}$) varies. Δ . The proportionality constants in these permeability relationships 4, 5 and 6 can be determined from a calibration experiment with a porous material of known porosity and permeability. The exponents n and m may vary depending on which of the above relations 4, 5 and 6 is used to determine the permeability. The values of n and m are not necessarily the same for each of the relationships. The porosity is determined by first running an NMR experiment with a water jacket which surrounds the radiofrequency probe (e.g. of the NMR logging tool) and therefore calibrates the NMR signal for 100% porosity. To prevent the interference from local radio signals one can enclose the probe and water jacket in a Faraday cage. As the NMR signal is directly proportional to the number of hydrogen nuclei in the sensitive volume of the probe it will scale linearly to lower porosities. Only the contribution from liquid phases or non-adsorbed fluid will be recorded if the dead time of the instrument is set accordingly. The temperature of the fluid in the sensitive volume is of secondary influence. In a bore hole environment this varies with depth and can be compensated for by measuring the bottom temperature and temperature gradient. The NMR signal amplitude changes as a function of temperature as $1/T$.

Detailed Description Text (11):

The magnetization of the fluid spins diffusing in the pore space satisfies the following modified Bloch equation: ##EQU2## $T.\text{sub.b}$ is the bulk relaxation rate of the fluid in the pore space and D is the diffusion constant which is on the order of $2.\text{times}.10.\text{sup.9}$ [$\text{m}.\text{sup.2} / \text{sec}$] for water at room temperature. The boundary condition is:

Detailed Description Text (12):

where ρ is the surface relaxation velocity, which has units of length over time and can be thought of as the relaxation rate at the surface multiplied by the thickness of the layer of fluid spins relaxing near the surface. The bulk relaxation rate can always be factored out of the solution.

Detailed Description Text (13):

The Bloch equation becomes: ##EQU3## Brownstein and Tarr [K. R. Brownstein and C. E. Tarr, Physical Review A, 19, 2446-2453 (1979)] expressed the general solution as a sum of normal modes: ##EQU4## Two limiting cases can be considered for the magnetization decay which are characterized by decay constants $\tau.\text{sub.c}$: ##EQU5## In the fast diffusion case the magnetization is approximately uniform across an isolated pore and only the lowest mode in the above eigenmode expansion contributes significantly to the magnetization decay. In this limit, $\rho.r/D \ll 1$, and when the pores are approximately isolated (narrow throat limit) one obtains for $m(t)$: ##EQU6## $S.\text{sub.p}$ and $V.\text{sub.p}$ are the surface area and the volume of a pore and $V.\text{sub.p} / S.\text{sub.p} \approx r$. For a pore size distribution the relaxation is described by: ##EQU7##

Detailed Description Text (14):

$r.\text{sub.c}$ is a lower cut-off on the pore size distribution. Thompson et al [see A. H. Thompson, S. W. Sinton, S. L. Huff, A. J. Katz, R. A. Raschke and G. A. Gist, Journal of Applied Physics, 65, 3259 (1989)] found that the pore size distribution of many porous rocks is well represented by the following class of functions:

Detailed Description Text (15):

and where Δ is a measure of the width of the pore size distribution and β lies between 0 and 1. A β value of $2/3$ will yield a Gaussian pore size distribution. This type of pore size distribution will lead to a stretched exponential decay in the fast diffusion limit:

Detailed Description Text (17):

Equation 16 is of a form observed experimentally for $T.\text{sub.1}$ and $T.\text{sub.2}$ magnetization decays for fluids in porous media for a broad set of experimental conditions, although it was derived for the case of surface induced relaxation. We wish to arrive at an expression which explicitly accounts for the contribution to the $T.\text{sub.2}$ decay from diffusion of fluid spins in porous media in the presence of internal magnetic field gradients. The magnetic field gradients lead to dephasing of

the nuclear spins which can only be partially compensated with a spin-echo sequence as they diffuse. As a starting point we use an expression derived by Robertson and Neuman and experimentally confirmed by Wayne and Cotts for the decay of the transverse magnetization in the presence of a uniform gradient G [see B. Robertson Physical Review, 151(1), 273 (1966), R. C. Wayne and R. M. Cotts, Physical Review, 151(1), 263 (1966), C. H. Neuman, The Journal of Chemical Physics, 60 (11), 4508 (1974)]. Neuman produced expressions for the case where the spins are assumed to diffuse in a bounded medium of spherical geometry and the Carr-Purcell spin-echo sequence with spacing of the π pulses given by τ . is being used: $\theta = 2\tau D/r$ and the α are determined from $\tan \alpha_i = 2\alpha_i / (2 - \alpha_i^2)$ whose solutions asymptotically approach: $\alpha_i = i \cdot \pi$. For small π the above expression agrees with the well-known expression for transverse relaxation of spins due to unrestricted diffusion in a uniform gradient:

Detailed Description Text (19):

$\Delta\chi$ is the susceptibility difference, μ_0 the magnetic permeability of vacuum and H_0 the magnetic field strength. This means that under this model the gradient is uniform over individual pores but varies from pore to pore. The contribution of the spins in each pore has to be weighted by the volume of the pore. For a pore size distribution we must average the magnetization decay, $m(t)$, over the pore size distribution in a fashion similar to the example in equation 14. We therefore arrive at the following expression for the contribution to the transverse magnetization of the spins diffusing in random internal gradient fields: $\sum_i \exp(-\alpha_i^2)$ where the last exponential explicitly accounts for the possibility of surface relaxation. This expression is the basis for numerical calculations performed for a series of pore size distributions. This expression was also previously, independently derived by Kleinberg and Horsfield [see R. L. Kleinberg and M. A. Horsfield, Journal of Magnetic Resonance, 88, 9-19 (1990)]. We numerically calculated the CPMG echo decay curve with the sum over the roots α_i being approximated up to the 20th term. The pore size distribution is of the form shown in Equation 15. The simulations were carried out in the same manner as the experiment. The CPMG decays were calculated for a set of values of τ . We observe that the calculated magnetization decays are well described by stretched exponential functions. This suggests that equation 16 applies to a broader class of relaxation decays than suggested by the derivation which only considered surface induced relaxation. Indeed the numerical results show that the decay of the magnetization due to diffusion in the presence of random magnetic field gradients and averaged over a pore size distribution also leads to stretched exponential decays.

Detailed Description Text (20):

FIG. 1a shows the pore size distribution calculated from equation 15 for typical values of $\Delta\chi$ and β . FIG. 1b shows the magnetization decay calculated for the pore size distribution of 1a from equation 20. This calculation was repeated for several values of τ and the nonlinear least squares fits to the stretched exponential function yield values for $T_{sub.2}$ and $\beta_{sub.2}$. FIG. 1c shows the $T_{sub.2}$ values thus obtained for a set of τ values.

Detailed Description Text (21):

Restricted diffusion can be expected at longer values of τ . The diffusion dynamics were therefore studied by systematically varying the parameter τ in the CPMG sequence. The crossover from free to restricted diffusion will then be evident in the dependence of both $T_{sub.2}$ and $\beta_{sub.2}$ on the diffusion time set by τ . CPMG experiments were repeated for a series of τ values. Values for $T_{sub.2}$ and $\beta_{sub.2}$ were obtained by non-linear least squares fits to a stretched exponential function for each coherence decay. For free diffusion is a linear gradient G the CPMG $T_{sub.2} \supset -1$ should be $\propto (G)^2 D \tau^2$, where D is the diffusion constant. For restricted diffusion D becomes effectively time dependent. To explain the τ dependence of $T_{sub.2}$ we use a model which interpolates between the limits of free diffusion considered above and restricted diffusion at long τ . The cross-over from unrestricted to restricted diffusion is well characterized by:

Detailed Description Text (22):

a result which was derived first in a pioneering paper by Stejskal on NMR measurements of restricted diffusion [E. O. Stejskal, Journal of Chemical Physics, 43, 3597-3603 (1965)]. $l_{sub.nmr}$ should be on the order of $V_{sub.p} / S_{sub.p}$, the volume-to-surface ratio of a pore. This gives a τ dependence for $T_{sub.2}$ of the form: $\sum_i \exp(-\alpha_i^2)$ This approximation for $T_{sub.2}$ (τ) leads to the correct limiting

behavior for τ .fwdarw.0. The experimental data points for $T_{sub_2}(\tau)$.sup.-1 fit well to the above equation. We observe that for typical parameters. 4D.sub.o τ ./l.sub.nmr.sup.2 <1. A power series expansion of equation 22 is therefore adequate as an approximation for $T_{sub_2}(\tau)$: ##EQU11##

Detailed Description Text (23):

The fit of equation 23 or 22 to the experimental $T_{sub_2}(\tau)$ data for several sandstone rocks are shown in FIG. 2. The fits to the experimental data yield coefficients for the two terms in the expression for $T_{sub_2}(\tau)$.sup.-1 of opposite sign as suggested by equation 23. The resulting values for l.sub.nmr are seen in FIG. 3 to correlate with a quantity l.sub.c derived from mercury injection. l.sub.c provides an estimate of the fluid flow permeability [see A. H. Thompson, S. W. Sinton, S. L. Huff, A. J. Katz, R. A. Raschke and G. A. Gist, J. Appl. Phys., 65(8), 3259 (1989)]. Therefore since l.sub.c is proportional to l.sub.nmr, l.sub.nmr provides an estimate of the fluid flow permeability. Mercury injection data indicate that the exponents n and m in equation 4 should be on the order of 2.0 .

Detailed Description Text (24):

Equation 22 is one approximation to the crossover from free to restricted diffusion and other expressions have been proposed in the literature. All have in common that they provide a characteristic length l.sub.nmr which is of relevance to determine the transport properties of the porous medium. The restricted diffusion analysis presented above is therefore not confined to the use of equation 22 but can be used for a variety of models describing the crossover from free to restricted diffusion. An example of an alternative model is equation 20 (used for numerical calculations), where the sum in the exponent can be used to define an effective diffusion coefficient. In each case the crossover from free to restricted diffusion is probed by measuring the τ . dependence of $T_{sub_2}(\tau)$ as outlined in this invention.

Detailed Description Text (26):

In actual practice the ability to determine the exact functional form which describes the τ . dependence of $T_{sub_2}(\tau)$ is limited by the time available for signal collection. This limits both the range of τ . values which can be measured and the signal-to-noise ratio of the data. However in each case there is a characteristic length which determines the dominant contribution to $T_{sub_2}(\tau)$. This length is related to the mean life time $\langle t \rangle$ for the magnetization decay. The mean life time is defined by [see D. J. Wilkinson, D. L. Johnson and L. M. Schwartz", Phys. Rev. B, 44, 4960-4973 (1991)]: ##EQU12## For stretched exponential decays the mean life time and T_{sub_2} from a nonlinear least squares fit to a stretched exponential are simply related: $\langle t \rangle = T_{sub_2} \cdot \text{GAMMA} \cdot (1/\beta_{sub_2})$ and for the range of β_{sub_2} values typical for magnetization decays in rocks the dependence of the mean life time on β_{sub_2} is weak. Using the approximation of free diffusion and with the assumption that the magnetic field gradient is inversely proportional to the pore radius the mean life time for the transverse magnetization decay is given by: ##EQU13## where $\delta \cdot \omega = \gamma \cdot G \cdot r$. $\text{apprxeq} \cdot \gamma \cdot \Delta \cdot \chi \cdot H_{sub_o}$. The free diffusion expression is a good approximation when T_{sub_2} is measured only for a limited set of short τ . values. Using equation 15 for the pore size distribution and a change of variable $((r/\Delta) \cdot \beta_{sub_2} / (1 - \beta_{sub_2}) = x)$, the mean lifetime is given by: ##EQU14## Significantly the mean life time and therefore also T_{sub_2} are directly proportional to Δ . and only weakly dependent on β_{sub_2} and r_{sub_c} / Δ . for typical values of these two parameters. This relation between T_{sub_2} and Δ . is a consequence of the pore size distribution. This result remains unchanged if we generalize the expression for the mean life time to include a different τ . dependence for $T_{sub_2}(\tau)$. This is evident by substituting a general functional dependence T_{sub_2} .varies. $F(\tau)$ in place of the T_{sub_2} .varies. τ .-.sup.2 in the above integral. ##EQU15##

Detailed Description Text (27):

Empirically we have observed that at a magnetic field of 7T and for the range of experimental τ . values used, the exponential function is a good approximation for $F(\tau)$. At other magnetic field strengths the simple exponential may not necessarily be a good approximation for $F(\tau)$. For the numerical simulations, we repeated the calculation of the $T_{sub_2}(\tau)$ data set for different pore size distributions where we arbitrarily changed Δ . and β_{sub_2} to change the shape of the pore size distribution. An exponential dependence of $T_{sub_2}(\tau)$ is seen to be also an excellent approximation for the numerically calculated results for $T_{sub_2}(\tau)$ as is evident from the example of FIG. 1c. For this case of a simple exponential dependence of $T_{sub_2}(\tau)$, the prefactor of the exponential is

equivalent to the value of $T_{sub.2}$ extrapolated to $\tau=0$. Thus the exponential extrapolation of $T_{sub.2}$ to $\tau=0$ is a measure of the prefactor of the exponential. We therefore expect that the extrapolated value of $T_{sub.2}$ to $\tau=0$ is proportional to Δ , and this is confirmed by numerical simulations as shown in FIG. 4.

Detailed Description Text (28):

The procedure of estimating Δ from the τ dependence of $T_{sub.2}$ either by prefactor analysis or extrapolation provides a simple estimate of the fluid flow permeability:

Detailed Description Text (29):

The proportionality of $T_{sub.2}$ ($\tau \rightarrow 0$) to Δ (and therefore $l_{sub.c}$) allows one to use $T_{sub.2}$ ($\tau \rightarrow 0$) to predict the fluid flow permeability from NMR measurements:

Detailed Description Text (33):

The method of this invention was tested in the laboratory using a nuclear magnetic resonance spectrometer whose functionality can replicate the capabilities of an NMR logging tool instrument. The samples used were sandstone core plugs from various geological formations in North America. For all porous samples we used the following procedure to prepare the samples: The samples were placed in a sealed container and imbibed with water. After imbibing a core plug with water for several hours it was taken out, sealed with Teflon tape and transferred to an NMR glass tube for measurements. In between measurements the samples were kept under water in a sealed container.

Detailed Description Text (34):

Several samples of sandstone rock were used in developing the present invention. The permeability and porosity of these samples was determined by standard methods. In addition on samples obtained from the same batch of rock cores mercury injection experiments were performed to determine a characteristic pore (throat) size $l_{sub.c}$. Mercury is a non-wetting fluid and under an applied pressure the mercury will first penetrate the largest pores of the medium. For a certain threshold pressure the first continuous path of mercury will be formed between the two ends of the sample and this will be detectable as a jump in the electrical conductivity across the sample. The length $l_{sub.c}$ can be calculated with the Washburn equation from the threshold pressure at which this first conducting mercury path is established across the sample. The values for permeability, porosity and $l_{sub.c}$ for the set of sandstone samples used for the NMR experiments are listed in Table 1. These values of permeability and $l_{sub.c}$ obtained independently from the NMR measurements will have to be compared with the predictions using $T_{sub.2}$ ($\tau \rightarrow 0$).

Detailed Description Text (35):

All laboratory NMR experiments were performed at a field strength of 7.05 Tesla corresponding to a Larmor frequency of the hydrogen nucleus of $\nu_{sub.L} = 300.13$ MHz. The $T_{sub.1}$ measurements were made with a standard inversion recovery pulse sequence. The $T_{sub.1}$ measurements were only made for completeness and are not important for the development of this invention. To acquire $T_{sub.2}$ data we use the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence which is comprised of an initial 90 radio frequency pulse which tips the longitudinal magnetization into the transverse plane. It is followed a time $\tau/2$ later by a train of 180 pulses with constant pulse spacing τ . At the midpoint between the 180 pulses the nuclear spin magnetization of stationary spins is refocused and a Hahn echo is formed. The echo will be attenuated for spins moving along the orientation of the magnetic field gradients. The magnetization is sampled at the center of the Hahn echoes. This means that for a train of n 180 degree pulses we acquire n data points. We repeat this experiment for a set of τ values. This procedure corresponds exactly to one outlined above in the section titled "Method of Invention". FIG. 5 shows a schematic diagram of the pulse sequence.

Detailed Description Text (36):

When measuring the $T_{sub.2}$ decay with the CPMG sequence as a function of pulse spacing, $T_{sub.2}$ decreases rapidly for porous samples imbibed with water or oil. By using the CPMG pulse sequence we can ascribe this decay of $T_{sub.2}$ to the effects of internal magnetic field gradients in the porous sample, which are mainly due to the magnetic susceptibility difference for the fluid imbibing the sample and the matrix. For most samples we recorded the decay of the transverse magnetization with the CPMG sequence for a set of 8-16 values of τ .

Detailed Description Text (38):

The $T_{sub.2}$ magnetization decays were fit to a stretched exponential function with a nonlinear least squares fitting procedure. FIG. 6 shows an example of the stretched exponential fit to a $T_{sub.2}$ CPMG decay curve. The stretched exponential function approximates the experimental data well over 2-3 orders of magnitude as can be seen from FIG. 6b. No data points were discarded before fitting the data to the stretched exponential function.

Detailed Description Text (39):

We acquired for each sample a set of CPMG decay curves by varying τ . The stretched exponential fit yields a value of $T_{sub.2}$ for each value of τ . The composite set of data point for $T_{sub.2}(\tau)$ is shown in FIG. 7 for three representative sandstone samples. We fit the resulting set of $T_{sub.2}(\tau)$ data to a single exponential function. FIG. 7 shows the nonlinear least squares fits as dotted curves. This allows one to extrapolate $T_{sub.2}(\tau)$ to $\tau=0$. $T_{sub.2}(\tau \rightarrow 0)$ should therefore give a value of the transverse magnetization relaxation time $T_{sub.2}$ independent of the strength of the internal magnetic field gradients and be proportional to some characteristic length of the pores. FIG. 8 shows a plot of $T_{sub.2}(\tau=0)$ versus the characteristic pore diameter $l_{sub.c}$ determined from the threshold pressure for mercury injection via the Washburn equation. Such a relationship is of great value for a rapid order of magnitude determination of permeability based on the above mentioned relationship proposed by Katz and Thompson: $k=1/126 l_{sub.c}^{sup.2} \phi_{sub.}^{sup.2}$. And indeed as FIG. 9 shows there exists a correlation between the product of porosity $\phi_{sub.}$ and $T_{sub.2}(\tau \rightarrow 0)$ and the independently determined permeability of the porous rock samples as predicted by the relation k varies. $[T_{sub.2}(\tau \rightarrow 0)]^{sup.2} \phi_{sub.}^{sup.2}$. In this equation the exponent of $T_{sub.2}(\tau \rightarrow 0)$ is predicted to be 2. However the range of the data in FIG. 9 would indicate that the exponent falls into a range of about 1.8 to 2.2. $T_{sub.2}$ values obtained with the CPMG pulse sequence (which should be the method of choice) are strongly dependent on the pulse spacing τ . Only when the gradient and diffusion induced relaxation is taken into account, do the resulting $T_{sub.2}(\tau)$ values extrapolated to $\tau=0$ show the discussed correlations with permeability and $l_{sub.c}$.

Detailed Description Text (40):

For the restricted diffusion analysis of $T_{sub.2}(\tau)$ we used a nonlinear least squares fitting algorithm to fit the experimental $T_{sub.2}(\tau)$ data to the expression of equation 22. The prefactor of τ in the exponent of the exponential is one of the adjustable parameters. $l_{sub.nmr}$ was directly determined from this adjustable fitting parameter obtained from the nonlinear least squares fit.

Detailed Description Text (41):

The present invention takes advantage of the correlations between $T_{sub.2}$ determined with NMR and a characteristic pore or throat size which determines the fluid flow permeability. This characteristic length $l_{sub.c}$ can also be determined by mercury injection but mercury injection experiments cannot be carried out in a down-hole environment. For in situ NMR relaxation time measurements in rock formations with an NMR logging tool it is feasible to carry out a $T_{sub.2}$ measurement described here with the present generation of logging tools and predict the fluid flow permeability using NMR in a manner which is much less time-consuming than other methods known to date.

Detailed Description Paragraph Equation (2):

$T_{sub.2}(\tau)$ varies. $\Delta/F(\tau)$ (2)

Detailed Description Paragraph Equation (14):

k varies. $T_{sub.2}(\tau \rightarrow 0)^{sup.m} \phi_{sub.}^{sup.n}$ (29)

Detailed Description Paragraph Table (1):

| TABLE 1 Sandstone samples and their porosity, permeability and $l_{sub.c}$ determined independently of the NMR measurements. | | | | | | | | | |
|--|-------------------------|--------------|-------------------|---------------|-------|------|------|--------------|----------------|
| sandstone type | $l_{sub.c}$ [μm] | porosity [%] | permeability [md] | | | | | | |
| Berea | 14.6 | 20.5 | 273 | Marsing No. 2 | 118.0 | 29.5 | | | |
| 54,000 Red Navajo | 23.5 | 23.6 | 1138 | Nugget | 10.77 | 10.9 | 4.16 | Silver No. 1 | 23.0 12.2 14.1 |
| Layered Navajo | 28.5 | 25.1 | 883 | Marsing No. 1 | 78.6 | 23.9 | 1276 | Silver No. 2 | 79.2 30.2 |
| 21,000 Table No. 2 | 91.6 | 24.1 | 3000 | | | | | | |

CLAIMS:

1. A method for determining the permeability of porous media saturated with a liquid using nuclear magnetic resonance (NMR) and comprising:
 - (a) applying a radiofrequency pulse sequence which after an initial pulse generates successive spin echoes with a train of radio frequency pulses spaced apart by a time interval of length τ , wherein all pulses have a carrier frequency corresponding to the Larmor frequency of the fluid spins filling the pore space of the medium for which the fluid flow permeability is to be determined;
 - (b) measuring the decay of the transverse magnetization at each of the successive regularly spaced midpoints between the 180 degree pulses where the midpoints coincide with the peak of the spin echoes;
 - (c) repeating steps a and b at least one more time wherein each repeat of step (a) uses said radio frequency pulse train with a different value of the pulse spacing τ ;
 - (d) determining the transverse relaxation time $T_{sub.2} (\tau)$, from the transverse magnetization decay for each value of τ , and determining one of a prefactor Δ , and a restricted diffusion length, $l_{sub.nmr}$, from said $T_{sub.2} (\tau)$;
 - (e) measuring the porosity of said porous media;
 - (f) determining the permeability of said media from the porosity and one of the prefactor Δ , and a restricted diffusion length, $l_{sub.nmr}$, from said $T_{sub.2} (\tau)$;
2. The method of claim 1 wherein said $T_{sub.2} (\tau)$ is of a form which includes an exponential function of τ .
3. The method of claim 2 wherein said $T_{sub.2} (\tau)$ is obtained from an expansion of the exponential functions.
4. The method of claim 2 wherein said $T_{sub.2} (\tau)$ is a simple exponential function of τ , and said prefactor Δ , is obtained by extrapolation of $T_{sub.2} (\tau)$ to $\tau=0$.
5. The method of claim 1 wherein said porous media is an earth formation and the measurement is performed in a well-bore environment with an NMR logging tool.
7. The method of claim 1 wherein the relaxation time, $T_{sub.2}$ is obtained from the transverse magnetization decay in step (d) by relating the transverse magnetization to time by a stretched exponential function.
13. The method of claim 11 wherein prefactor Δ , is determined as prefactor of the observed $T_{sub.2} (\tau)$ dependence.
14. The method of claim 4 wherein said permeability of step (f) is obtained from the product of the porosity and the extrapolated transverse relaxation time, $T_{sub.2}$ at $\tau=0$.
15. The method of claim 14 wherein said porosity and the extrapolated transverse relaxation time, $T_{sub.2}$ at $\tau=0$ are each raised to a power.

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L21: Entry 6 of 6

File: USPT

Dec 6, 1994

DOCUMENT-IDENTIFIER: US 5370901 A

TITLE: Compositions for increasing the image contrast in diagnostic investigations of the digestive tract of patients

Brief Summary Text (2):

The present invention concerns innocuous ingestible or enterally administrable compositions which, depending on the contrast agent incorporated thereto, can be used as contrast enhancer media for imaging, on the first hand in ultrasonic echography, and on the second hand, in nuclear magnetic resonance imaging (NMRI), both of the gastro-intestinal tract of animal and human patients.

Brief Summary Text (5):

It is also well known that NMRI techniques comprise subjecting a patient to a main static magnetic field combined with a linear gradient magnetic field, both being directed to some parts of the body to be investigated. The magnetic fields act on the nuclei of atoms with fractional spin quantum numbers and encode them into various degrees of statistical alignment with different resonant frequencies in a selected direction of orientation; the nuclei of concern here are mainly that of hydrogen atoms, i.e. protons, these being predominantly that of molecules present in relatively high concentration in or around the organs to be investigated, viz, the protons of water and lipids. For doing the measurements, one will apply to the parts of the body under investigation pulses of radio-frequency that matches with the resonance energy of the protons involved in the tissues or fluids of said parts of the body. When the protons under consideration are excited by a pulse of resonant energy, they are raised to a higher energy state which causes them to flip from the average orientation direction controlled by the magnetic field. Thereafter, the protons will return to their original state by relaxation in an exponential time dependent fashion, the corresponding energy then reemitted (spin-echo) forming a response signal typical of the protons under consideration, i.e. depending on their immediate environment.

Brief Summary Text (6):

NMRI techniques are actually based on the detecting, acquiring and electronically processing of this signal (according to Fourier transforms) and thereafter displaying it spatially on a screen, thus forming an image whose various patterns correspond to areas having protons in different environments, i.e. to protons belonging to organ tissues or body fluids being subjected to investigation.

Brief Summary Text (7):

Among the critical factors pertaining to MRI, one usually distinguishes two mutually perpendicular components of the proton-distinctive relaxation time parameter, namely the spin-lattice component along the axis of magnetization (called T_{sub.1}), which corresponds to the release of energy to the nuclear environment, and the perpendicular or transverse (spin-spin) relaxation component (called T_{sub.2}), that corresponds to the returning of the nucleus to the initial statistical energy level. Either T_{sub.1} or T_{sub.2} can contribute to the definition of the NMR images depending on the kind of organ selected and the measurement conditions.

Brief Summary Text (8):

It should be noted that when the measurements are carried out in the absence of agents added for increasing image contrasts, the differences in relaxation time constants between protons in various parts of the organs are small and the image is of poor to bad quality. The contrast effect can however be enhanced by the presence, in the environment of the hydrated molecules under excitation, of a variety of

magnetic species, e.g. paramagnetic (which mainly affect $T_{sub.1}$) and ferromagnetic or superparamagnetic (which mainly affect the $T_{sub.2}$ response). The paramagnetic substances include some metals in the ionic or organo-metallic state (e.g. $Fe_{sup.+3}$, $Mn_{sup.+2}$, $Gd_{sup.+3}$ and the like, particularly in the form of chelates to decrease the intrinsic toxicity of the free metal ions). Ferromagnetic contrast substances preferably include magnetic aggregate particles of micronic or submicronic size, i.e. not smaller than about 100-200 nm, for instance particles of magnetite ($Fe_{sub.3} O_{sub.4}$), γ - $Fe_{sub.2} O_{sub.3}$, ferrites and other magnetic mineral compounds of transition elements. Superparamagnetic materials are usually very small magnetic particles (below about 100-150 nm) which, because their size is under a critical value, do not behave any longer as small autonomous magnets, i.e. they will align in a preferential direction only when subjected to an external magnetic field. The advantage of the superparamagnetic materials (also defined sometimes as superparamagnetic fluids) over the ferromagnetic particles is mainly of efficiency density, i.e. being smaller, the number of available magnetic particles for a given weight of metal is greater in the case of superparamagnetic particles than with ferromagnetic particles and the magnetic efficiency on the neighboring protons is further enhanced.

Brief Summary Text (13):

It has been indicated above that paramagnetic contrast agents in which the metals are in the ionic state or in the form of metal-organic compounds are often metabolizable and toxic and, although this toxicity can be controlled to some extent by using very strong chelatants and non-metabolizable polymer carriers, it is desirable to further minimize possible hazards by using less toxic materials, e.g. non-metabolizable magnetic particles of sufficient size not to diffuse through the intestinal membrane; the micronic ferromagnetic and nanometric superparamagnetic aggregate particles typically fulfill such requirements. For instance, in U.S. Pat. No. 4,770,183 (ADVANCED MAGNETICS), there is recommended to use biodegradable sub-micron sized superparamagnetic metal oxide particles (1-50 nm) which may be used uncoated or coated with a polysaccharide (like dextran) or serum albumin. Coating is effected by precipitating the particles with alkali, starting with water solutions of metal salts in the presence of the polymer. These products are suitable for intravenous applications as well as for gastrointestinal applications, in which case they are administrable by intubation or enema, presumably because otherwise biodegradation by the stomach fluids would be too fast and toxicity might become a problem.

Brief Summary Text (14):

In WO85/04330 (NYCOMED), there is disclosed the use of ferromagnetic particles as contrast agents for NMRI. As mentioned before, ferromagnetic particles are bigger than superparamagnetic particles and behave as small permanent magnets which also achieve a significant reduction of $T_{sub.2}$. For direct administration into the digestive tract, the ferromagnetic particles are preferably embedded in a cellulose matrix or coated with this matrix. Cellulose derivatives can also be added as viscosants but the reference indicates that contrast enhancement is not readily achieved beyond the stomach, presumably because the embedding cellulose matrix does not protect sufficiently the particles from attack by the stomach fluids. Non-biodegradable embedding or coating matrices are therefore recommended to minimize absorption of toxic materials by the body.

Brief Summary Text (15):

EP-A-186.616 (SCHERING) discloses the use of complexes of particles of magnetite ($Fe_{sub.3} O_{sub.4}$), γ -iron oxide ($Fe_{sub.2} O_{sub.3}$) and metal ferrites as contrast agents for NMRI. The cited complexants include oligo- and polysaccharides, proteins, polycarboxylic acids, protective colloids and other compounds. Examples of such compounds comprise polyvinyl-alcohol (PVA), polysilanes, polyethylene-imine, dextran, dextrin, oleic acid, gelatin, globulin, albumin, insulin, peptides and antibodies. The particles can also be encapsulated in liposomes. For enteral administration, the contrast agents are suspended in a water medium which may contain further ingredients such as salt or excipients like methylcellulose, viscosants, lactose, mannitol and surfactants like lecithin, Tween.RTM., Myrj.RTM. and the like.

Brief Summary Text (18):

After testing the compositions of the cited prior art consisting of coated or uncoated magnetic particles in admixtures with polymer carriers, the present inventors noted that the contrast effect in NMR imaging is generally unstable and rapidly vanishes, presumably because despite the presence of the carrier phase the

magnetic particles tend to coalesce or coacervate together under the influence of the external magnetic field which strongly reduces their controlling effect on the spin-relaxation of the neighbouring protons. They however also found that such undesirable coalescence of the magnetic particles and vanishing of the $T_{sub 2}$ relaxing effect can be prevented by either selecting as the carrier phase substantially water-insoluble hydrophilic water-swelling substrates which tend to form gels with water or, when using water-soluble polymer carriers, raising the pH of the aqueous medium containing the magnetic particles to at least 13 when admixing with the polymer solution, and keeping the dry weight ratio of said polymers to magnetic particles not below 5:1 and, preferably, in the range of 100:1-10:1.

Brief Summary Text (19):

Although the exact reason of these findings is not definitely explained, it can be postulated that using carrier matrices which form nearly insoluble gels upon admixing with water (thixotropic or pseudo-plastic solutions) will locally raise the viscosity at the particle/carrier interface to such extent that the particle mobility is impeded and agglomeration is prevented.

Brief Summary Text (22):

The foregoing findings form the basis of the present invention as recited below and in the annexed claims, i.e. the invention mainly concerns diagnostic compositions to be used as contrast enhancing agents, on a first hand in the imaging by echography, and on a second hand in the NMR imaging, of portions of the digestive tract of humans and animals, said compositions comprising, depending on the needs, i.e. on the kind of investigation, at least one member of a group consisting of two types of contrast enhancing particles, viz. magnetically and ultrasonically responsive particles, in admixture with, or chemically bonded to, at least one physiologically acceptable carrier phase. The said carrier phase is substantially water insoluble, although swellable by hydration and gel forming, and, when hydrated, has differential affinity for the gastro-intestinal mucosa, i.e. it adheres preferably to some areas thereof, thus forming luminal linings or coatings having specific magnetic contrast response patterns which enable improved visualization of specific portions of the oeso-gastro-duodenal tract.

Brief Summary Text (23):

The carrier phase of the present composition can be selected from water-soluble polymers which can form homogeneous solutions in aqueous media, in which case the proportion of signal generating particles therein preferably not exceeds 10% by weight of solution, more preferable 5%, for optimized stability against coalescence when subjected to a steady magnetic field. The polymers which are convenient are for instance dextran, polyvinyl-pyrrolidone (PVP), carboxymethyl-cellulose (CMC) and the like. It is quite surprising that, contrary to products of the prior art with a high particle/carrier weight ratio, homogeneous dispersion of magnetic particles in relatively low concentrations in the carrier polymer remain stable in a magnetic field with virtually no or very little agglomeration of the magnetic particles, and hence no substantial weakening of the imaging response under the conditions of NMR imaging. Although the compositions with water-soluble polymers have no recognized specific affinity for the internal mucosa membrane of the digestive tract, they are useful for controlling the transit therethrough of the magnetic particles, either alone or when preferably used in association with bioadhesive carrier phases.

Brief Summary Text (25):

These carriers have the general property to get hydrated with water and form therewith substantially insoluble gels which strongly adhere to the membrane mucosa. Depending on the selected carrier phase, the compositions of the invention can be made to have controllable transit time through the gastrointestinal tract and particular adhesion to selected portions thereof, thus enabling efficient NMRI of selected organs. Normally, the compositions using polymer carriers having no or little bioadhesion will permit faster transit than the compositions using carriers with strong bioadhesive character, hence controlled transit can be achieved with compositions in which non-bioadhesive and bioadhesive carriers are admixed in suitable proportions. It has also been surprisingly found that the particular selection of carriers used in the compositions of the invention, i.e. the carriers with enhanced affinity for mucosa membranes at low pH and/or soluble carriers with high dispersive capacity for magnetic particles, provide generally excellent transverse and longitudinal luminal imaging homogeneity.

Brief Summary Text (26):

One preferred type of bioadhesive polymers to be used as the carrier phase in this invention is a polymer or copolymer of acrylic acid containing a proportion of other monomers (generally di- or polyfunctional allyl ethers or acrylates) to impart a degree of oil-water-insolubility and swelling capacity to form gels. Suitable polymers of this type are available on the market under the names oil Carbopol.RTM. or Polycarbophil.RTM., for instance from the Goodrich Company. Other suitable polymers of comparable type are disclosed in EP-A-309.404 (included for reference) and comprise copolymers of acrylic acid with allyl ethers of glycols or sugars. Upon addition of water these polymers will form viscous dispersions of microgels which have strong affinity for internal mucous membranes. Furthermore, the gelling and swelling properties of such polymers are pH dependent; hence the volume, bulk and adhesive properties of the carrier can be controlled by adjusting the pH to a desired value.

Brief Summary Text (27):

The present ingestible NMRI contrast compositions are stable even at pH 1 and this is another advantage over similar products of the prior art as they are not attacked by stomach fluids which normally dissolve magnetite particles into Fe.sup.+2 and Fe.sup.+3 ions. This is obviously undesirable for both toxicity and imaging efficiency reasons. Bioadhesivity is particularly effective under acid or near neutral conditions; at high pH the bioadhesivity is decreased and may become negligible. Hence control of bioadhesivity by pH control is another asset of the present invention.

Brief Summary Text (28):

For manufacturing the contrast compositions according to the invention one usually admixes the signal generating particles (the echogenic or magnetically responsive particles, or both) with the carrier phase. In regard to the MRI aspect of the invention, one may use magnetic particles which can be ferromagnetic or superparamagnetic. The nature of both and the distinction between them has been stressed before in this specification. Hence, one prefers superparamagnetic particles for optimized density efficiency, i.e. magnetic particles of size not exceeding about 150 nm and preferably in the 1-100 nm range (10-1000 Å). The preparation of such magnetic particles is well known and disclosed in many references, e.g. the aforementioned references and further references, e.g. U.S. Pat. No. 4,554,088; EP-A-125.995 (Advanced Magnetics); U.S. Pat. No. 4,267,234; U.S. Pat. No. 4,157,323 (California Institute); WO-A-78/00005 (Mosbach); WO-A-83/01738; WO-A-83/03426; WO-A-84/00294 (Schroder). They are also available commercially, e.g. from Ferrofluidics Corp., Burlington, Mass. They normally result from the alkalization of an aqueous solution containing Fe.sup.+2 and Fe.sup.+3 salts in correct proportions.

Brief Summary Text (30):

In one embodiment of a method for preparing the compositions according to the present invention, an aqueous suspension of the magnetic particles is treated with alkali to raise the pH to 13 or more, then the obtained alkaline suspension is admixed with an aqueous solution or dispersion of the carrier phase at the same pH and finally a water-compatible organic solvent in which the carrier phase is insoluble is added, whereby a precipitate of the desired composition is formed. The composition can thereafter be separated, for instance by filtration, and washed free from alkali, then it can be stored dry. When used for internal NMRI investigation, the composition can be rehydrated with water or an aqueous solution of innocuous excipients, this being for oral or enteral administration.

Brief Summary Text (31):

In the foregoing embodiment, the magnetic particles are not covalently linked to the carrier phase, the latter being water-soluble, but still they are immobilized therein presumably due to the existence of electrostatic or Van der Waals forces between the carrier phase constituents and the magnetic particles or, if the carrier is insoluble in water but in hydrated gel form, to immobilization of the hydrated magnetic particles within the carrier gelled structure.

Brief Summary Text (34):

For using the present compositions as an echogenic or NMRI contrast agent (or both) in the study of the digestive tract, the compositions (when stored dry) are admixed with an aqueous phase suitable for oral administration in order to provide a gel which will adhere to a predetermined extent to the mucous membrane of the digestive tract and therefore will carry the particles through said tract to the portion thereof to be visualized. The rate of transfer and the transit time can be adapted

by properly selecting the nature and degree of bioadhesion of the carrier phase. For this, variable proportions of contrast compositions including water-soluble carrier polymer can be admixed with the bioadhesive carrier, these proportions being selected to reach up to 99% by weight or more in the case where little restricted transit, unrestricted transit or accelerated transit is desired. For instance, for NMR investigations, using mainly dextran as the carrier phase in rats gave a transit rate similar to that observed with no carrier, while using mainly CMC as carrier gave accelerated transit. Using Carbopol.RTM. as the carrier phase gave strongly retarded transit, particularly in the duodenum portion of the intestinal tract. The present contrast compositions may also advantageously comprise isoosmolarity agents which minimize loss or gain of water during intestinal transit, i.e. diffusion by osmosis; such agents may comprise carbohydrates such as sorbitol, mannitol, xylitol and the like.

Detailed Description Text (3):

A water solution (30 ml) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (185.3 mg; 0.685 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (80.5 mg; 0.405 mmol) labeled with ^{59}Fe was brought slowly to pH 13.4 by the dropwise addition of 3% aqueous NH_4 solution; then it was heated to 75.degree. C. for about 10 min. This resulted in the formation of a dark brown suspension of magnetite in large and coarse particles.

Detailed Description Text (4):

To this was added under agitation a solution of 5 g of Dextran in 200 ml of water and the pH was readjusted to 13.4 by adding some more NaOH solution. After 15 min more stirring, alcohol was added, whereby a very fine precipitate of Dextran-magnetite was formed. This precipitate was drained under suction, washed with alcohol and dried at 50.degree. C. in air.

Detailed Description Text (6):

The proton magnetic resonance transverse relaxivity, expressed as R_2 , i.e. $R_2 = 1/T_{2\text{sub}} / \text{mmol Fe}$ was measured on aqueous dispersions of the aforementioned precipitate by means of a 60 MHz RMN spectrometer. The measurements were effected at mid-height of the absorption peaks. Values of R_2 in the range of 500-550 (mM.s) $^{-1}$ were obtained which did not substantially change with time, thus showing that reagglomeration of the particles did not occur.

Detailed Description Text (9):

To a solution of Dextrin (80 g) in 180 ml of H_2O at 70.degree. C. were added a solution of 19 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (70 mmol) and 7.01 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (35 mmol) in 105 ml of water. A tracer quantity of $^{59}\text{FeCl}_3$ was also added. The pH was raised to 2.4 by first adding 20% aqueous Na_2CO_3 , then it was brought to pH 11 with 10N NaOH added dropwise, whereby the color of iron oxides developed. The mixture was refluxed for 30 min, then it was cooled to room temperature and the pH was brought to 6.2 with 6N HCl. Then 0.8 liter of ethanol was added which caused the formation of a precipitate. This was collected, resuspended in water and the suspension was dialyzed for 24 hrs in running water (membrane cut-off=10'000). Then the suspension was freeze-dried which gave a blackish powder.

Detailed Description Text (10):

Measurements of R_2 as described above gave none or useless responses. Analogous results were obtained by replacing Dextrin by a comparable amount of Dextran. Obviously, the ratio of metal to polymer in this formulation is much too high to prevent reagglomeration of the particles subjected to a magnetic field.

Detailed Description Text (13):

To a solution of 13.56 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (50 mmol) and 5.3 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (27 mmol) in 60 ml of water labeled with ^{59}Fe (about 10 μCi) were added dropwise 60 ml of 5M aqueous NaOH until the pH was above 13. The solution was left to stand until a blackish sediment accumulated at the bottom of the container. This was washed carefully by decantation ten times with portions of 300 ml H_2O . After the last portions, the pH of the water had dropped to 9.3.

Detailed Description Text (15):

Sixty ml of glycerol were added and the mixture was heated under reduced pressure in a rotavapor until a black viscous residue has formed. This residue was diluted with 240 ml of water, agitated for 20 min and allowed to rest whereby it separated into two phases. This was dialyzed for 24 hrs against a citrate buffer (10 mM, pH 8.3 with ammonia) in order to remove low molecular material (glycerol, unreacted silane

and acrylate oligomers).

Detailed Description Text (16):

A suspension was made containing 20 ml of acrylic acid 10 ml H.sub.2 O and 10 ml of the silanized magnetite prepared as described above. This suspension was heated to 50.degree. C. and a 10% aqueous ammonium persulfate solution was added dropwise. After the polymerization was complete, the polymer was ground in 500 ml of water and dialyzed against running water. Then it was freeze-dried to give 20.1 g of silvery powder.

Detailed Description Text (17):

A suspension of 1 g of this powder in 100 ml of water was prepared and 1 ml of this suspension was mixed with 9 ml of a 1% aqueous solution of Carbopol R at DH 7-8. The relaxation time T.sub.2 was measured as described in Example 1, the value found being R.sub.2 =160 (s.mM).sup.-1.

Detailed Description Text (20):

The Table provides the names of the polymers, the yield of the preparation (calculated on the basis of the iron converted to magnetite) and the relaxivity R.sub.2 in terms of s.sup.-1 mmol

Detailed Description Text (24):

Samples of the suspensions (0.1 ml) were diluted with 9.9 ml (dilution 1:100) of 1% by weight aqueous polymer solutions also containing 0.3 mol/l of mannitol to preserve isotonicity. The polymers used were:

Detailed Description Text (25):

a) Carboxymethylcellulose (CMC) Na salt (0.1 g/9.9 ml of water).

Detailed Description Text (29):

e) Control; this was made as above by diluting the magnetite preparation to 1/100 but using only water without polymer.

Detailed Description Text (30):

Five ml of samples a) to e) were administered to Sprague-Dawley rats (about 180 g) which were kept fast except for water 24 hrs before administration. The samples were introduced intragastrically with a ball-point syringe. The tracer amount in each sample accounted for about 10.sup.6 cpm.

Detailed Description Text (36):

A 3% aqueous solution of NH.sub.4 OH (about 25 ml) was slowly added dropwise under agitation to a 100 ml water solution of 619.2 mg of FeCl.sub.3.6H.sub.2 O (2.29 mmol) and 262.1 mg of FeCl.sub.2.4H.sub.2 O (1.32 mmol). The mixture was then heated to 75.degree. C. for 10 min. There were thereafter added 200 ml of an aqueous 2.5% by weight solution of sodium alginate and the pH was raised to 13.5 with 40% aqueous NaOH. After further agitating for 15 min at room temperature, alcohol was added to precipitate the magnetite-polymer composition; the powder was drained on a filter, washed with alcohol and dried; the yield was 4.96 g containing 0.216 mmol of Fe (theory=0.22 mmol). The mmolar transverse relaxivity R.sub.2 was measured at 60 MHz on a water suspension of the powder with a perkin-Elmer/Hitachi NMR apparatus. The measured value was R.sub.2 =465 (s.mM).sup.-1.

Detailed Description Text (39):

The magnetite suspension was allowed to come back to room temperature, the pH was lowered to 6.5 with 1N HCl and there were added two grams of aluminum-sucrose-octasulfate (sucralfate) sold under the name of Keal.RTM. by Laboratories SINBIO, 75116 Paris (France). The mixture was diluted with 50 ml H.sub.2 O and further agitated for 10 min after which it was left to stand, whereby a precipitate of magnetite-sucralfate settled at the bottom of the vessel. This was drained on a filter, washed with water and dried, yield 2.03 g. R.sub.2 (in water)=283 (s.mM).sup.-1.

Detailed Description Text (43):

Montmorillonite clay of the Beidel type (BEDELIX.RTM.) available from Laboratories Beaufour, 28100 Dreux (France) was tested for NMRI contrast response under the following conditions: three g of BEDELIX.RTM. were stirred in 100 ml of a 0.5% solution of Carbopol.RTM.. The 1/T.sub.2 value of this preparation was measured as usual with a Perkin-Elmer/Hitachi NMR apparatus at 60 MHz and found to be 435.5 s.sup.-1 without the addition of magnetite. This value was stable (due to the

presence of the Carbopol.RTM.) and the preparation could be used as such for the NMRI of the digestive tract of animals.

Detailed Description Text (45):

A suspension of magnetite was prepared as disclosed in Example 1, first paragraph. A 0.2 ml portion of this suspension was added to 99.8 ml of a 0.5% by weight solution of Carbopol.RTM.. The iron concentration in this preparation was 0.178 mmol/ml; the $1/T_{sub.2}$ value was 144.5 s.^{sup.-1}, i.e. $R_{sub.2} = 812$ (s.mM).^{sup.-1}.

Detailed Description Text (46):

Aliquots of the magnetite preparation were taken and to each were added a different quantity of BEDELIX.RTM.. The $R_{sub.2}$ values were measured as usual and reported below in function to the % by weight of added BEDELIX.RTM..

Detailed Description Text (49):

Male Sprague Dawley rats were used for the experiment after 24 hours of fasting. Eight ml of the Carbopol-magnetite solution were administrated orally to the conscious animals which were anesthetized 10 min later by 30 ml/kg of Pentotal. Transversal MR images were then taken on an Esaote ESATOM 5000 imager equipped with a special 8 cm i.d. RF receiver coil, using a slice of 2 mm, a F.O.V. of 15.9.times.15.9 cm, and a matrix size of 128.times.256. $T_{sub.2}$ weighted images (SE 200/70/1), were acquired as well as $T_{sub.1}$ weighted images (SE 500/16/2), and intermediate scan images (SE 350/50/2). For the T_2 weighted and intermediate scan images gradient moment hulling techniques were used in order to minimize respiratory artifacts. The T_2 weighted and intermediate scan images show a clear delineation of the darkened and expanded bowel loops. Especially the 350/50/2 image showed very clearly the single loops of the small intestine. The wall of the loops could be clearly observed. A cross section of the colon and of a kidney were also seen as well as abdominal and dorsal muscles. The contrast media was distributed evenly over the whole GI tract.

Detailed Description Text (51):

A suspension of echogenic microballoons was prepared as described in Example 4 of reference EP-A-458 745 using poly-L-lactic acid (commercially available under the name of Resomer.RTM. R-207 from Boeringer Ingelheim, Germany). There was obtained a suspension of microballoons in distilled water (concentration 10.^{sup.9} /ml; average size 5.2 .mu.m).

Detailed Description Text (52):

On the other hand, an aqueous suspension of gelled bioadhesive polymer was prepared by dispersing 1% by weight of Carbopol.RTM. resin (Goodrich Company) in water. The pH of this suspension was brought to 13 with concentrated NaOH and to 100 ml of the alkalized solution were added 10 ml of the aforementioned microballoon suspension. After homogenizing the mixture under agitation, a quantity of ethanol was added sufficient to precipitate the solids; the polymer was drained on a filter under suction, washed with alcohol and dried under vacuum. The dry powder was then resuspended in 100 ml of a 0.3 M mannitol aqueous solution and the pH adjusted to 3-4 with HCl.

Detailed Description Paragraph Table (3):

| | % of BEDELIX .RTM. $1/T_{sub.2}$ (s. ^{sup.-1}) |
|--|--|
| $R_{sub.2}$ (s .multidot. mM). ^{sup.-1} | 0.5 163.4 |
| 918 1 251.3 1412 1.5 402.1 2259 | |

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L22: Entry 1 of 1

File: PGPB

Jan 9, 2003

PGPUB-DOCUMENT-NUMBER: 20030009297

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|-----------------------|---------|-------|---------|---------|
| Mirotnich, Konstantin | Calgary | | CA | |
| Allsopp, Kevin | Calgary | | CA | |
| Kantzas, Apostolos | Calgary | | CA | |
| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| | | | | | | | | | |
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☐ 1. Document ID: US 20030009297 A1

L23: Entry 1 of 6

File: PGPB

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PGPUB-DOCUMENT-NUMBER: 20030009297

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DOCUMENT-IDENTIFIER: US 20030009297 A1

TITLE: Determination of oil and water compositions of oil/water emulsions using low field NMR Relaxometry

PUBLICATION-DATE: January 9, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
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| Marentette, Daniel | Calgary | | CA | |

US-CL-CURRENT: 702/25

| | | | | | | | | | | |
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☐ 2. Document ID: US 20020167314 A1

L23: Entry 2 of 6

File: PGPB

Nov 14, 2002

PGPUB-DOCUMENT-NUMBER: 20020167314

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20020167314 A1

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

PUBLICATION-DATE: November 14, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
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US-CL-CURRENT: 324/303

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 3. Document ID: US 6512371 B2

L23: Entry 3 of 6

File: USPT

Jan 28, 2003

US-PAT-NO: 6512371

DOCUMENT-IDENTIFIER: US 6512371 B2

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

DATE-ISSUED: January 28, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
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| Prammer; Manfred | Downington | PA | | |

US-CL-CURRENT: 324/303

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 4. Document ID: US 6140817 A

L23: Entry 4 of 6

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 5. Document ID: US 5387865 A

L23: Entry 5 of 6

File: USPT

Feb 7, 1995

US-PAT-NO: 5387865

DOCUMENT-IDENTIFIER: US 5387865 A

TITLE: Permeability determination from NMR relaxation measurements for fluids in porous media

DATE-ISSUED: February 7, 1995

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------------|-------------|-------|----------|---------|
| Jerosch-Herold; Michael | High Bridge | NJ | | |
| Thomann; Hans | Bedminster | NJ | | |

US-CL-CURRENT: 324/303; 324/300

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Draw Desc | Image | | | | | | | | | |

☐ 6. Document ID: US 5370901 A

L23: Entry 6 of 6

File: USPT

Dec 6, 1994

US-PAT-NO: 5370901

DOCUMENT-IDENTIFIER: US 5370901 A

TITLE: Compositions for increasing the image contrast in diagnostic investigations of the digestive tract of patients

DATE-ISSUED: December 6, 1994

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|--------------------|----------|-------|----------|---------|
| Tournier; Herve | Valleiry | | | FR |
| Hyacinthe; Roland | Douvaine | | | FR |
| Cavagna; Friedrich | Vicenza | | | IT |

US-CL-CURRENT: 427/2.12; 424/9.5, 427/2.14, 436/173

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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| Draw Desc | Image | | | | | | | | | |

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| TEMPS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 79432 |
| TEMPERATURES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 655826 |
| HEAT\$4 | 0 |
| HEAT.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2400792 |
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| HEATABL.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1 |
| HEATABLE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 11855 |
| HEATABLY.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 33 |
| (L21 AND (TEMPERATURE OR HEAT\$4)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 6 |

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